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REDUCING CHLORIDE CORROSION OF STAINLESS STEEL IN THE NUCLEAR FUEL MANUFACTURING INDUSTRY: AN ELECTROCHEMICAL-ENVIRONMENTAL PERSPECTIVE

Ву

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A thesis presented to Ryerson University in partial fulfillment of the requirement for the degree

of

Master of Applied Science

In the program of Environmental Applied Science and Management

Toronto, Ontario, Canada

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ABSTRACT

Chloride extraction from nitric acid is an important technique for reducing corrosion of stainless steel. However, there has been a limited amount of research conducted in this area. Pumping ozone-enriched air through nitric acid is a corrosion reduction method that is widely used in the nuclear fuel manufacturing industry, including the Blind River Refinery (BRR), to purge chlorine gas out of the acid. However, this method has been shown to produce significant environmental impacts. Overall, it is an inconsistent and cost-deficient method for reducing chloride corrosion of stainless steel in nitric acid mediums below 7.2M (37.0% volume). This thesis builds on existing literature and demonstrates that oxidizing chloride ions in nitric acid using oxygen, nitric oxide and nitrous oxide is an efficient and cost-effective chloride extraction method for the case study (BRR). It was shown that the level of chloride extraction from nitric acid increased significantly when the acid strength was elevated above 8.4M (42.0% volume) and sparged with various oxidants. The most effective oxidants at this nitric acid strength were: oxygen, ozone, nitric oxide and nitrous oxide. Nitric oxide and nitrous oxide can be produced by sparging 43.0% nitric acid with air or sparging 43.0% nitric acid with NOx fumes. In terms of the BRR case study, it was shown that using operational-specific combinations of these methods can drastically reduce the environmental impacts associated with their chloride removal process; significantly increase the level of chloride extraction; reduce energy consumption and operating costs by as much as 54.0%; and reduce material requirements by as much as 80.0%.

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1.0 Introduction

1.1 Corrosion in the Nuclear Manufacturing Industry Overview

Corrosion treatment methods have been applied in many nuclear fuel manufacturing facilities in an effort to counterbalance corrosion damage and reduce the associated environmental impacts [1]. Despite recent technological advances in corrosion prevention, corrosion still remains a significant operational, environmental, health, safety and cost issue for nuclear fuel manufacturing facilities [2]. Improving corrosion prevention may not solely depend on developing newer technology, but rather improving methods and technologies that already exist. This goal can be achieved by utilizing resources that are already in place to cost-effectively reduce the level of corrosion and improve environmental, health and safety conditions.

Corrosion is generally described as a chemical or electrochemical reaction between a material (most often metal) and its surrounding environment that ultimately produces a deterioration of that material and its properties [3]. There are various types of corrosion that exist. In the nuclear fuel manufacturing industry, the most prevalent form of corrosion is the corrosion of metals [4]. Nuclear fuel manufacturing process areas are largely composed of various grades of stainless steel, such as 304 and 316-stainless steel, which are susceptible to corrosion. The most common types of metallic corrosion of stainless steel in these areas are [4]:

- general corrosion;
- pitting corrosion;
- crevice corrosion; and
- stress corrosion cracking (SCC).

General corrosion of metals, such as metallic valves, pipes and tanks, in nuclear fuel manufacturing facilities is often observed over a long-term period. The time period for corrosion to occur can range from several weeks to several decades depending on the nature of the materials present and the operating conditions. Electrochemical oxidation of these metals occurs as they are exposed to oxygen or strong acids over a long period of time [5]. Metals containing high iron contents are most susceptible to corrosion. The formations of iron oxides and iron oxide-hydroxides (rusts) are one of the most commonly observed forms of metallic corrosion in a nuclear fuel manufacturing facility [6].

Pitting and crevice corrosion are two other types of corrosion that are of concern in nuclear fuel manufacturing facilities, especially for passivated stainless steel [7]. The corrosion resistance of stainless steel is accomplished through passivation, whereby an outer oxide layer acts as a protective barrier to corrosive oxidation. It works by preventing the transfer of electrons between materials [8]. Pitting and crevice corrosion often occur in a low oxygen environment or in the presence of significant concentrations of oxidizing agents such as chlorides [9]. As discussed previously, strong acid pipes and holding tanks in nuclear fuel manufacturing facilities are most often composed of passivated grades of stainless steel, such as 304 and 316-stainless steel. Depending on the location of these pipes and tanks, failure of these metallic structures is dangerous for both the environment and on-site workers. The presence of a strong acid in small crevices produced by pitting and crevice corrosion provides the low pH required to deteriorate stainless steel [10]. The nature of strong acids is a serious health risk and poses severe environmental threats to soil, groundwater, river and lake water, vegetation, terrestrial and aquatic organisms [11]. Temperature is also an important factor, along with the pH and oxygen level, for determining the level of crevice and pitting corrosion of a stainless steel structure [12]. Many processes within nuclear fuel manufacturing facilities operate at high temperatures. Elevated temperatures are detrimental, since they increase the rate of metallic corrosion [13].

Stress corrosion cracking (SCC) is another form of corrosion that is particularly problematic in the nuclear fuel manufacturing industry [14]. Although there are numerous similarities between SCC, pitting and crevice corrosion, SCC tends to be more chemically specific [14]. Chlorides, for example, compete as anions on the surface of stainless steel and often interfere with the stainless steel alloy's ability to re-form a passive film in a few localized areas [15]. Stainless steel alloys in these areas degrade as a result of auto-catalytic oxidation (low oxygen and pH) and produce small pits in the affected material [16]. This type of corrosion is the most dangerous form of corrosion in nuclear fuel manufacturing facilities, since it often occurs in strong acid mediums (hydrochloric, nitric, and sulfuric) and goes undetected until the damage is irreparable [17]. Figure 1 illustrates the chemical mechanism of SCC by way of chloride ion interference on the surface of a stainless steel alloy.



Figure 1: Stress Corrosion Cracking: Chloride ions prevent the transfer of electrons and the reformation of a passivated oxide layer on the surface of stainless steel structures [16].

Corrosion reduction systems carry an environmental burden. The energy required to operate corrosion reduction technologies, such as chloride removal systems using ozone generation, is substantial. The resources required to repair the damage caused by corrosion, such as repairing and replacing metallic structures, also indirectly adds to the associated environmental impacts [18]. Therefore, reducing corrosion is not only cost-beneficial, but also environmentally beneficial when taking into consideration the energy and materials required to mitigate the issue. This thesis will attempt to exemplify the idea of using current corrosion reduction theories and methodologies and applying them in a case study on Cameco Corporation's Blind River Refinery (BRR), located in Blind River, Ontario. Also, researching and applying current corrosion reduction theories and methods to the BRR will identify the current gaps and limitations that may exist regarding current theories and methods, and build on these limitations to provide a greater understanding of pertinent corrosion reduction theory for future industrial and academic research.

1.2 Problem Statement

The primary operational concern associated with the current process at the BRR is continuous corrosion of stainless steel structures and lines in the nitric acid recovery circuit due to elevated concentrations of chloride in the nitric acid. Corrosion is a problem throughout the refinery, but is most acute in the nitric acid absorbers and concentrators (see Section 3.2.2 and 3.2.3). The current chloride removal system uses an ozone generating system to oxidize chloride ions in the nitric acid recovery circuit to chlorine gas. A

purge system is in place to remove the chlorine gas from the acid (see Section 3.2.4). There are several problems with the current system. The first major problem is the cost issue associated with the current chloride removal circuit. The amount of energy required to operate the system, in relation to the amount of chloride being removed from the circuit, is very high. The total amount of energy used in 2009 amounted to 50,550 kW [19] compared with a 49.0% average level of chloride extraction for the same year [20]. The level of chloride extraction is too low, in terms of cost-efficiency, and has become a liability for the BRR. In terms of environmental impacts associated with the energy use of the current chloride removal circuit, the relative amount of carbon dioxide emitted in 2009 from the energy production fed to the Ontario Power Grid to meet this energy requirement was calculated to be approximately 4.55×10^5 kg.

The maintenance and repair costs required for the chloride removal and nitric acid circuits were also very high. The total costs in 2009 for the chloride removal circuit and the nitric acid circuit were \$39,984.02 and \$229,496.16 respectively; this includes materials and labour [21][22]. The material requirements for the repairs associated with corrosion, as well as the structural damage and malfunctions that cause ozone, NOx and nitrates/nitrites to escape into the environment will also be considered in the following research (these issues will be discussed in further detail in section 3.0).

1.3 Purpose

The purpose of this thesis is to develop a more efficient and cost-effective chloride removal system for the BRR's nitric acid recovery circuit in order to reduce the chloride corrosion of stainless steel tanks and lines. It will be demonstrated that an effective alternative chloride removal system can be applied to existing conditions at the BRR that will reduce the costs associated with repairs and maintenance to the chloride removal and nitric acid circuits. The purpose is also to reduce the environmental impacts that are associated with the current chloride removal system. This research will seek to apply current corrosion reduction theories and methods to a specific case study, as well as build on corrosion reduction theories and methods that currently exist. While the thesis is specifically focused on corrosion reduction at the BRR, it is anticipated that the results will be of interest to both academics and practitioners in corrosion reduction.

1.4 Scope

The scope of this thesis will focus on a variety of chloride corrosion reduction theories and methods that are currently being used or researched in the nuclear fuel manufacturing industry and other industries alike. The scope will also include a thorough study of the BRR and all of the operations associated with this research. Thereafter, the most applicable alternative chloride removal theories and methods will be tested at the BRR using conditions that resemble those in the nitric acid and chloride removal circuits.

1.5 Objectives

The primary objective of this research is to develop a more cost-efficient chloride removal circuit at the BRR. A second objective is to reduce the environmental impacts associated with the energy demands of the current chloride removal system, as well as the maintenance and repair costs associated with the continuous corrosion problem in the nitric acid and chloride removal circuits. The goal is to find an effective alternative oxidant(s) that can reduce chloride concentrations more efficiently, consistently and cost-effectively. A final objective will be to provide new practical and theoretical information regarding chloride extraction that can build on previous literature and provide further information for future industrial and academic research.

1.6 Organization of the Thesis

The thesis is organized as follows:

Literature Review: This section will provide a review of literature regarding corrosion reduction methods and theories. A thorough review of pertinent literature will be used to identify potential corrosion reduction methods and theories that can be applied to the BRR (i.e., corrosion reduction theories and methods dealing with chloride corrosion of stainless steel). Also, applicable chloride corrosion reduction methods and theories will be analyzed in order to discover gaps and limitations in the current literature, as well as investigate applicable concepts that can be used to expand the current knowledge about chloride corrosion reduction and offer insight for future academic research in this area. Methodology: This section will present the strategy of inquiry developed for this thesis, as well as describe the methods used to test various chloride corrosion reduction methods investigated during this research. This section will also provide a detailed description of the BRR.

Results and Discussion: This section will present the results obtained during the tenure of this research. The results for each alternative developed during this research will be discussed in order to identify the electrochemical processes involved, the positive and negative effects for the BRR associated with each alternative, and new discoveries that can be used to build on existing literature.

Conclusions and Recommendations: This section will provide a summary of the results obtained during this research and discuss their significance for the BRR and academia. Based on the results of this research, a recommendation(s) will be presented for the BRR. Thereafter, a summary of contributions to the BRR and academia (i.e., new discoveries that can build on gaps and limitations in current literature) will be provided.

2.0 Literature Review:

2.1 Introduction

As discussed in section 1.0, there are many forms of corrosion that occur in the nuclear fuel manufacturing industry [13]. As a result, there have been many proposed corrosion reduction methods developed for different environments. In order to determine which literature on corrosion reduction methods applies best to the operational conditions at the BRR, a thorough review of pertinent literature was conducted. The goal of the literature review was to explore as many corrosion reduction practices as possible that are potentially applicable to the conditions at the BRR. Thereafter, the most applicable literature was used to develop theoretical and methodological approaches for applying an alternative chloride removal system at the BRR. The literature review also includes a presentation of important electrochemical and chemical kinetic principles for various proposed chloride removal methodologies that will be explored during this research.

2.2 Survey of Key Literature

There are a number of methods that have been developed and applied in an attempt to reduce the amount of corrosion in nuclear fuel manufacturing facilities [13]. In particular, four methods have been identified to be applicable at the BRR. These methods include:

- materials resistance to corrosion [13];
- corrosion inhibitors [23];
- protective coatings [26]; and
- chloride ion elimination [28].

2.2.1 Method 1: Materials Resistance to Corrosion:

The most widely used corrosion preventation method in the nuclear fuel manufacturing industry is selecting materials resistant to corrosion [24]. Unfortunately, there are no materials that are completely resistant to corrosion. As previously discussed, SCC is prevalent in the nuclear fuel manufacturing industry due to the wide use of strong acids and high temperature environments. Chloride corrosion is a major source of SCC of stainless steel [16]. Only small concentrations of chloride ions are required to produce dramatic corrosion effects on stainless steel, especially in the presence of a strong acid such as nitric acid [25].

The concept that Kolman presents for the case of materials resistance to corrosion is a measure that has been taken as a first step at the majority of nuclear fuel manufacturing facilities, including the BRR. The most common method used in the nuclear fuel manufacturing industry is selecting stainless steel metal compositions that are generally more corrosion resistant [13]. Stainless steel alloys are often composed of higher grades of nickel or zinc to be more anti-corrosive. Also, stainless steels used in the nuclear fuel manufacturing industry are often passivated stainless steel to further increase their resistance to corrosion [26]. Selecting materials that are both functional in the facility process environment and resistant to corrosion should always be the first corrosion prevention step taken at any industril facility. Although there are financial costs related to corrosion resistant materials, the payoff outweighs the initial costs in a relatively short amount of time. As discussed previously, no material is completely resistant to corrosion. As a result, materials selection is only the first step to preventing corrosion in the nuclear fuel manufacturing industry.

2.2.2 Method 2: Corrosion Inhibitors:

Corrosion inhibitors are not commonly used in nuclear fuel manufacturing facilities; however, they are are particularly important for nuclear power plants [22]. Therefore, they have been included as a potential corrosion reduction method for this research.

Heat exchangers in nuclear power plants are susceptible to multiple forms of corrosion (i.e., general corrosion, SCC, crevice corrosion, and pitting corrosion). The temperature across these aluminum heat exchangers can reach as high as 1100°C [22]. Under these thermal conditions, the rate of corrosion is drastically increased [23]. This has a negative effect on the durability and efficiency of heat exchange, as well as safety threats to the surrounding environment. Radioactive corrosion and fission products from the primary coolant of the nuclear core reactor can leak into the secondary cooling loop through holes in the heat exchanger. These radioactive corrosion by-products can then enter the surrounding water as secondary cooling water flows through the cooling cycle [27].

One method for reducing corrosion in heat exchangers is by applying an electrophoretic coating using epoxy resin and a spraying of polyurethane with addition of metallic pigments. This type of coating is classified as a corrosion inhibitor, since it disallows the transfer of electrons through the electrolyte between the anode and cathode materials [27]. Although this option is viable for preventing the interference caused by chloride ions on the surface of stainless steel structures, it is limited in its use in the nuclear fuel manufacturing industry due to the use of strong acids. Nitric acid would readily degrade epoxy resins applied to stainless steel in the nitric acid recovery circuit at the BRR. As a result, this corrosion prevention method is not a suitable alternative for the BRR.

2.2.3 Method 3: Protective Coatings:

Another method for reducing the susceptibility of stainless steel to corrosion is by applying a protective coating [28]. There are numerous types of coatings that can be applied to reduce the susceptibility of corrosion, such as:

- organic coatings (e.g., paints or powder coatings);
- inorganic coatings (e.g., zinc rich paints or phosphates);
- conversion coatings (e.g., chromates or phosphates); and
- metallic coatings:
 - mechanically applied zinc as in mechanical plating;

- electrolytically deposited metals, zinc for functional purposes or decorative nickel/chromium for decorative purposes; and
- o electroless deposited metals such as nickel.

Similarly to the use of corrosion inhibitors, protective coatings do not perform well in strong acid environments at elevated temperatures, since protective coatings are also easily dissolved and degraded [29]. This is an important limitation for the application of anti-corrosive coatings at the BRR. As a result, it is not a suitable candidate for this research.

2.2.4 Method 4: Chloride Ion Elimination

Chloride corrosion of stainless steel can occur by way of SCC, crevice corrosion and/or pitting corrosion [13]. These types of corrosion are particularly important in the refining of uranium ores in the nuclear fuel manufacturing industry. Nitric acid is a common diluting agent used in refining uranium ores to secondary products (e.g., uranium trioxide), which renders stainless steels in these environments more prone to various forms of corrosion. As previously discussed, metallic coatings and corrosion inhibitors are often ineffective due to the fact that they are degraded in a low pH environment. Thus, chlorides in the presence of nitric acid present a unique corrosion problem that must be dealt with in a different way than typical metallic corrosion [30].

There has been limited research in electrochemical chloride removal from nitric acid, since research has been primarily focused on chloride removal from steel reinforced concrete due to its susceptibility to corrosion (especially in marine environments). Electrochemical removal of chloride from steel reinforced concrete involves an embedded cathode (i.e., the steel within the concrete specimen) and an external anode immerged in an electrolyte. A direct current (DC) is applied and chloride ions (both free chloride and bound chloride) slowly migrate towards the cathode [32]. Although this approach is useful for steel reinforced concrete, its application for removing chloride from nitric acid is unsuitable due to the nature of ions existing in aqueous form (i.e., nitrate ions would be removed from the nitric acid solution). As a result, cathodic removal of chloride is not a suitable option for chloride extraction from nitric acid.

The use of ozone generation as a means to oxidize chloride in nitric acid has several problems: high maintenance costs; high capital costs for operation; and inconsistent chloride oxidation [31]. As discussed in Section 1.2, these issues are also present within the current chloride removal circuit at the BRR. In terms of suitbable alternatives, Wilkinson (1961) notes that there are three possibilities for reducing chloride corrosion of stainless steel in the presence of nitric acid [31]:

- discarding a chloride-contaminated acid stream;
- removal of chlorides via precipitation/filtration; and/or
- removal of chlorides via oxidation to chlorine gas.

Discarding a chloride-contaminated acid stream is not a viable option, since it can be very costly over the long-term and would likely disrupt the nitric acid balance within a facility. The removal of chlorides by precipitation/filtration is a more applicable option. It requires the use of materials that absorb chloride ions without absorbing nitrate ions from the nitric acid solution, which would be unbeneficial to the nuclear fuel manufacturing process. Materials such as chromium can be used as chloride absorbents to reduce the overall chloride concentration in nitric acid and, as a result, reduce the level of SCC of stainless steel [8]. The removal of chlorides by a precipitation/filtration system is a viable option; however, the risk of absorbing nitrate ions and secondary products essential to the nuclear fuel manufacturing process renders this option less desired. The most applicable chloride extraction method for the nuclear fuel manufacturing industry is the oxidation of chloride ions using strong oxidants (e.g., ozone and NOx gases).

Recent research performed at the Savannah River National Laboratory in South Carolina revealed that chloride can be effectively oxidized to chlorine gas in nitric acid using nitrogen dioxide [33]. The experiments were performed at various hydrochloric/nitric acid concentrations to determine whether chloride was removed from acid solutions due to the nature of the strong acid or due to the use of nitrogen dioxide gas sparging. A series of tests were performed with solutions containing variable nitric and hydrochloric acid concentrations in the absence of nitrogen dioxide gas, as well as a separate range of tests applying a constant flow of nitrogen dioxide gas through the solution. In summary, they found that chloride ions that were produced from the dissolution of hydrochloric acid could only be moderately oxidized to produce chlorine and nitrosyl chloride gases. Chlorine gas was the dominant gas produced when the acid strength of the solution was above 12 M (for both tests – with and without a constant flow of nitrogen dioxide gas was the dominant gas produced when the acid strength of the solution was above 12 M (for both tests – with and without a constant flow of nitrogen dioxide gas.) Nitrosyl chloride gas could only be produced when a constant flow of nitrogen dioxide was sparged through the solution. For acid concentrations ranging from 5-10 M the dominant gas produced was chlorine gas [33]. Again, this reaction required a constant flow of nitrogen dioxide through the solution. The basic reactions are as follows:

$$3\text{HCl}(l) + \text{HNO}_3(l) \rightarrow \text{ClNO}(g) + \text{Cl}_2(g) + 2\text{H}_2\text{O}(l)$$
(1)

$$Cl^{-}(l) + 2NO_{2}(g) \rightarrow ClNO(g) + NO_{3}^{-}(l)$$

$$(2)$$

The most effective chloride oxidation using nitrogen dioxide occurred for acid solutions above 6 M (25.0% volume). It is important to note that nitrogen dioxide is not a strong enough oxidant to oxidize chloride ions to chlorinated gases (see Section 2.3). The oxidation of chloride ions in the acid solution occurs as a result of the formation of nitric oxide, which is a strong oxidant (see Section 2.3.3). Nitric oxide is produced when nitrogen dioxide reacts with water [33]:

$$3NO_2(g) + H_2O(l) \rightarrow 2HNO_3(l) + NO(g)$$
 (3)

Pierce et al. (2007) observed that effective extraction of chloride was a direct function of initial acid concentration. As the concentration of acid increased, so did the relative rate of chloride oxidation. Pierce et al. (2007) also found that reaction 1 occurred more prominently in the presence of nitrogen dioxide gas, since the reaction occurred significantly more at 6 M in the presence nitrogen dioxide compared to the same concentration in the absence of nitrogen dioxide. In terms of temperature dependence, the chloride oxidiation reactions presented above were slightly amplified at elevated temperatures. Pierce et al. (2007) compared the same experiments at 20°C and 70°C and noticed that chloride removal was higher in strong acidic solutions (6-8 M) at 70°C [33].

It is important to note that the stoichiometry of the chloride oxidation reactions observed by Pierce et al. (2007) did not match the observed oxidation levels (i.e., greater amounts of chloride were oxidized than predicted by the molar ratio of reactions versus products). Thus, based on the nature of the experiments performed, there was a gap in their results that could not explain the additional oxidation of chloride. This gap was investigated during this research and is discussed in Section 4.1.3.

The principle of oxidizing chloride ions in nitric acid to chlorinated gases is a similar approach to the ozone generation chloride removal system that is currently being used at the BRR. The main differences between the methods are the cost-effectiveness of chloride removal and the consistency by which it is removed. The ozone generation removal system is inconsistent in terms of chloride removal yields. The experiments undertaken by Pierce et al. (2007) demonstrated a high level of chloride removal consistency in strong acids sparged with nitrogen dioxide. Based on the results provided by Pierce et al. (2007), a similar method may potentially be applied to the BRR that would be more efficient and cost-effective than the current method.

2.3 Electrochemical Principles of Chloride Oxidation

2.3.1 Oxidation of Chloride Ions Using Ozone

The current chloride removal circuit removes chloride ions in the absorber nitric acid as it passes through three chloride reactors (discussed in Section 3.2). The ozone generator produces ozone-rich air (0.5-1.0% ozone), which is sparged through eductor pumps at the bottom of each chloride reactor [34]. The chemical mechanism for chloride removal is oxidation of chloride ions to chlorinated gases (primarily chlorine gas). Oxidation is defined as the loss of an electron(s) or the gain of an oxygen molecule from a particular molecule or ion [35]. A strong oxidant is required to strip the electrons from the chloride ions, since chlorine is a strong oxidant itself:

$$Cl_2(g) + 2e \Rightarrow 2Cl^{-}(aq)$$
 $E^{\circ}(V) = 1.360$ (4)

 E° (V) is the oxidation-reduction potential (ORP) of chlorine gas measured in volts. It represents the electric voltage produced by the transfer of electrons. Therefore, in order for the reaction to go to the left (i.e., oxidation of chloride ions) it requires an oxidant that has an ORP greater than 1.360 V to strip the electrons from the chloride ions. There are not many oxidants that have an ORP greater than 1.360 at the BRR. The only possible oxidants are: ozone, nitric oxide, nitrous oxide and oxygen. The current chloride removal circuit uses ozone as an oxidant [34]:

$$O_3(g) + 2H^+(aq) + 2e \Rightarrow O_2(g) + 2OH^-(aq)$$
 $E^o(V) = 2.421$ (5)

Ozone has a high enough ORP (greater than chlorine) to oxidize chloride ions in a ratio of one mole of ozone to two moles of chloride. An electron from each chloride ion is stripped by the ozone molecule and chlorine gas is produced as a result [35].

2.3.2 Oxidation of Chloride Ions Using Oxygen

One of the proposed alternatives for the chloride removal circuit is to pump dry air through nitric acid circulating through the chloride reactors (see Section 3.3). Oxygen composes roughly 16.0% of air being pumped into the circuit [34]. Nitric acid strength plays a critical role for oxidizing chloride ions using oxygen. A strong acidic environment (low pH) will have a much higher concentration of hydrogen ions. Increasing nitric acid strength from 35.0% to above 43.0% would provide a much greater concentration of

hydrogen ions. The ORP for oxygen in an acidic environment varies according the pH. As the pH lowers, the ORP for oxygen increases [35]:

$$O_2(g) + 2H^+(aq) + 2e \Rightarrow H_2O_2(l)$$
 $E^o(V) = 0.695$ (6)

This environment would not provide the ORP required to oxidize chloride ions to chlorine gas, since the ORP of chlorine (1.360 V) is far greater than the ORP of oxygen. Lower pH levels are beneficial for oxidation. In a strong acid medium, such as one provided by strong nitric acid, the ORP of oxygen increases [35]:

$$O_2(g) + 4H^+(aq) + 4e \Rightarrow 2H_2O(l)$$
 $E^o(V) = 1.229$ (7)

As shown in reaction 7, the ORP of oxygen is 1.229 V in 1.0 M nitric acid. However, the ORP value is significantly higher at concentrations greater than 1.0 M. The fact that 36.0% nitric acid has a hydrogen concentration of 7.0 M; it is conceivable that the ORP value of oxygen in this acidic medium would be far greater than 1.229 V. The ORP of chlorine is not affected by the concentration of hydrogen ions (as shown in reaction 4). Therefore, increasing the acid strength would increase the relative ORP of oxygen without increasing the ORP of chlorine simultaneously [35].

2.3.3 Oxidation of Chloride Ions Using Oxides of Nitrogen (NOx)

Nitric acid above 40.0% in the presence of moisture begins to fume by producing small amounts of oxides of nitrogen (NOx) such as: nitric oxide (NO), nitrogen dioxide (NO₂), nitrous oxide (N₂O) and dinitrogen tetraoxide (N₂O₄). Depending on the relative concentrations of these NOx gases, the fumes can have a light-reddish color all the way to a dark-reddish brown color. NOx gases, most importantly nitric oxide and nitrous oxide, are highly oxidative. Nitric oxide and nitrous oxide have the following ORP values at 1.0 M [35]:

$$2NO(g) + 2H^{+}(aq) + 2e \Rightarrow N_{2}O(g) + H_{2}O(l) \qquad E^{\circ}(V) = 1.591$$
(8)

$$N_2O(g) + 2H^+(aq) + 2e \Rightarrow N_2(g) + H_2O(l)$$
 $E^{\circ}(V) = 1.766$ (9)

Therefore, the ORPs of both nitric oxide and nitrous oxide are sufficient to oxidize chloride ions, since they are well above the ORP of chlorine gas. The ORP of nitrogen gas is negligible, since it is well below that of chlorine. The OPRs for nitrogen dioxide and dinitrogen tetraoxide are also well below that of chlorine. Therefore, they would not be a source of oxidation for purging chlorides out of a nitric acid solution.

The ORP values provided are for 0.50 - 1.0 M acidic conditions. The pH environment in the nitric acid circuit is far more concentrated than 1.0 M (ranges from 6.0 - 9.0 M). As a result, the low pH environment will be beneficial for the ORP values of NOx, oxygen and ozone, since chlorine is not affected by the concentration of hydrogen ions. As the environment becomes more acidic, the ORP values of NOx, oxygen and ozone would increase relative to chlorine [35].

High temperatures are also beneficial for oxidation due to the fact that electrons are more easily stripped from chloride, since they are more unstable at elevated temperatures [8]. Therefore, the operating conditions in the nitric acid circuit favor oxidation of chloride ions using NOx and oxygen. Also, the current chloride removal circuit sparges ozone-rich air into the circuit with only 0.50 - 1.0% of the air being composed of ozone. Nitric oxide and nitrous oxide fumes will compose greater than 1% of NOx being sparged into the nitric nitric acid.

Pure nitric acid emits white fumes. This is due to the fact that it contains less than 2.0% water and 0.50% nitrogen dioxide [35]. The white fumes emitted from pure nitric acid are almost entirely gaseous nitric and nitrous acids. Gaseous nitric acid has a negligible ORP and nitrous acid has an ORP slightly below that of chlorine [35], as shown by reaction 10:

$$2HNO_2 (l) + 4H^+ (aq) + 4e \Rightarrow N_2O (g) + 3H_2O (l) \qquad E^{\circ} (V) = 1.297$$
(10)

However, as discussed previously, the ORP value will be significantly higher in 6.0 - 10.0 M nitric acid [35]. As a result, any nitrous acid gas fumes dissolved in the nitric acid could potentially oxidize chloride ions present in the acid.

2.3.4 Effect of Trace Metals (and Other Factors) on Oxidizing Chloride Ions

The ability to oxidize dissolved chloride ions to chlorine gas in a nitric acid solution must also consider trace concentrations of other elements in the solution. As discussed previously, chlorine is a strong oxidant and, as a result, has a high ORP value (1.360 V). Any element present in the nitric acid containing a lower ORP value than chlorine will be oxidized first by all of the oxidants discussed in the previous section. The following table demonstrates the electrochemical series for various trace metal ORP values:

Equilibrium	ORP Value as E° (volts)
K+(aq) + e- <u> </u>	-2.92
Ca ²⁺ (aq) + 2e ⁻ Ca(s)	-2.87
Na⁺(aq) + e⁻ Na(s)	-2.71
Mg ²⁺ (aq) + 2e ⁻ Mg(s)	-2.37
Al ³⁺ (aq) + 3e ⁻ Al _(s)	-1.66
Zn ²⁺ (aq) + 2e ⁻ Zn(s)	-0.76
Fe ²⁺ (aq) + 2e ⁻ Fe _(s)	-0.44
Pb ²⁺ (aq) + 28 ⁻ — Pb _(s)	-0.13
2H⁺ _(aq) + 2e ⁻ <u> </u>	0
Cu ²⁺ (aq) + 2e Cu _(s)	+0.34
Ag*(aq) + e- — Ag(s)	+0.80
Au ³⁺ (aq) + 3e ⁻ — Au(a)	+1.50

Table 1: Electrochemical Series of Trace Metals: The table above indicates the oxidation-reduction potentials (ORPs) for various trace metals. The elements with lower ORP values are more easily oxidized. Therefore, the oxidation potential decreases from top to bottom [35]. The only element having a higher ORP value than chlorine under standard conditions is Gold (Au).

2.3.5 Chemical Kinetics

The ability of oxidants to oxidize chloride ions to chlorine gas is not only governed by the ORP, but also the activation energy required for the reaction to occur. By definition, activation energy is the minimum energy required for a chemical reaction to occur [35]. Reactant molecules come together and chemical bonds are stretched, broken, and formed to give rise to the products of the reaction. During this chemical reaction, the energy of the system increases to a maximum and then decreases to a minimum to give rise to the products. As shown in Figure 2, the activation energy is the difference between the maximum energy and the energy of the reactants [35].



Figure 2: Activation Energy Diagram: The diagram displays an exothermic reaction. The amount of energy released is displayed by delta H. The activation energy is the minimum energy required for the reaction to take place [35].

The activation energy determines the way in which the rate of the reaction varies with temperature. The activation energy is governed by the Arrhenius equation [36]:

$$\ln K = \ln A - Qc/RT \tag{11}$$

Rearranging the Arrhenius equation to solve for Ea gives:

$$Qc = (\ln K - \ln A) / RT$$
⁽¹²⁾

Where K is the rate of a given constant; A is the pre-exponential factor; Qc is the activation energy; R is the gas constant; and T is the temperature. The pre-exponential factor (A) is determined experimentally [36].

The Arrhenius equation is important for determining the changes of reaction rates as temperature is increased or decreased [36]. The alternative chloride removal circuit proposal would operate at roughly the same temperature as the current circuit. Therefore, the effect of rate changes will be negligible. The important consideration from the Arrhenius equation is the activation energy to determine whether the oxidation reactions will occur. Determining the pre-exponential factors in order to determine the activation energies of equations 3-9 is a complex procedure that requires laboratory tools and methods beyond the scope of this research. Also, the ratio of various NOx gases is difficult to measure in order to

determine which oxidants are more dominant. Therefore, for the purposes of this study, the level of chloride extraction from the laboratory experiments using strong nitric acid and sparging will provide evidence to assume that there is a sufficient amount of activation energy for the oxidation reactions to occur.

2.3.6 Nitric Acid Strengths and Concentrations

It is important to understand the conversions between molarity, normality and nitric acid strength. Nitric acid is a strong acid and has one equivalent hydrogen ion per mole [35]:

 $HNO_{3}(l) \rightarrow H^{+}(aq) + NO_{3}^{-}(aq)$ (13)

Therefore, nitric acid molarity (mol/L) and normality (equivalents of solute per litre of solution) are the same [35].

Nitric acid strength is a measurement of the volumetric percentage of nitric acid in the total solution [35]. There is a conversion chart between normality and nitric acid strength in the analytical procedure BRR:CAM:HNO3:3 [37]. This chart is used for the determination of free acid in process samples as well. A nitric acid strength – normality chart is provided in Table 2.

Normality (N)	Vol. %HNO3
5.62	30
5.84	31
6.05	32
6.29	33
6.51	34
6.74	35
6.97	36
7.20	37
7.44	38
7.67	39
7.91	40
8.15	41
8.39	42
8.64	43
8.88	44
9.13	45
9.38	46
9.63	47
9.88	48
10.1	49

Table 2: Nitric Acid Normality and Acid Strength Conversion Chart: The nitric acid strength ranges used in the research vary between 30% and 49%. Therefore, the conversion chart for the associated normality is provided. It is important to note that the normality and molarity are the same for nitric acid [37]. This will be important for comparing nitric acid strength to nitric acid concentrations provided in the key literature.

2.4 Motivation for Research and Anticipated Benefits

The energy and maintenance costs associated with corrosion have been significant and are a recognized opportunity at the BRR. Also, the cost-efficiency of the chloride removal circuit has been questioned in the past several years. The level of chloride extraction in comparison to the overall cost of the circuit renders it one of the most cost-deficient circuits at the BRR. The environmental and operational impacts of the current removal system can be improved simultaneously. This has lead to the motivation to apply an alternative chloride removal circuit that is more cost-efficient, environmentally and operationally beneficial to the BRR and the local environment.

One of the main anticipated benefits of applying an alternative chloride removal circuit is reducing the overall energy consumption required to operate the current chloride removal circuit. This will indirectly provide an environmental benefit, since reducing energy consumption will also reduce the relative amount of carbon dioxide emissions from retrieving energy from the provincial power grid. Applying a more effective chloride removal circuit at the BRR will reduce the maintenance costs required for corroded stainless steel systems in the refinery. This is due to the fact that a greater level of chloride extraction would reduce the overall concentration of chlorides throughout the entire refinery. Improving the environmental impacts associated with ozone emissions from the current chloride removal circuit is another anticipated benefit if the current chloride removal system is replaced with an alternative system.

As previously discussed, there has been limited research concerning chloride induced corrosion in nitric acid and, more importantly, chloride extraction methods from nitric acid. Effectively extracting chloride from nitric acid can provide financial, structural and safety benefits to a wide range of industries. Also, identifying the gaps and limitations in the literature regarding chloride extraction methods can benefit future industrial and academic research in similar areas. Although extracting chloride from nitric acid may seem to be specific to certain industries and operating conditions, it is anticipated that the electrochemical principles applied to this research can be of particular use for future academic research in the area of chloride oxidation and corrosion prevention.

3.0 Methodology

3.1 Strategy of Inquiry

A combination of existing and new data was used during the research. Daily samples of nitric acid from the bottom of the lead nitric acid absorber and the denitration scrubber tank were taken (see Section 3.2). These locations were sampled daily from Monday to Friday during the period of May – August 2010. Samples for the nitric acid absorber B were taken from the bottom of the absorber, since this is the safest and most accessible sample location. Previous data results were collected from the BRR internal data input system, which resides on the AS 400 computer system. This is a computer data input program that includes concentration results from lab analyses for elements and compounds of interest at the refinery. There is a vast amount of data from the past 20 years that has been logged and is easily accessible. However, this research focused on data collected in 2009 in order to focus on the more recent trends of chloride concentrations. Data regarding chloride compound concentrations, NOx concentrations out the absorber stack and nitrate/nitrite levels in the plant effluent discharge were also collected for this time period.

Lab tests provided new data from collected nitric acid samples. The concentrations of chloride in nitric acid were determined by using the analytical produce for the Cary 100 UV-visible spectrometer [38]. The nitric acid samples were then prepared for UV-visible spectrometer according the absorptiometric determination procedures provided in the BRR laboratory [39]. Coincidentally, the acid strength of the nitric acid samples taken was determined using the "determination of free acid in process samples procedure" [40].

3.2 Case Study

3.2.1 Blind River Refinery

The case company is Cameco's Blind River Refinery (BRR). Cameco Corporation is one of the world's largest uranium producers. The BRR is part of Cameco's Fuel Services division and is the world's largest commercial uranium refinery with a capacity to produce up to 18,000 tonnes of uranium trioxide per year. BRR receives uranium ore concentrate from various uranium mines worldwide and refines the

concentrate into uranium trioxide, which is then shipped to the Port Hope Conversion Facility or the Springfield Fuels Facility for further processing [41].

3.2.2 General Uranium Refining Process Overview

As shown in Figure 3, digestion is the first stage of the uranium refining process at the BRR. In the digestion area, there are two digestion vessels. To start the process, uranium ore concentrate is continuously fed into the first digestion vessel where it is dissolved in nitric acid. The solution then enters the second digestion vessel, where it is conditioned with phosphoric acid. The resulting slurry is pumped through extraction feed lines to the next stage in the process: solvent extraction. There are three solvent extraction columns. In the first column, uranium is extracted from the slurry by a kerosene/tributyl phosphate organic phase. The aqueous phase from the first column is drained into raffinate holding tanks while the 'loaded solvent' flows into a second and third column focused on scrubbing and re-extraction respectively. The resulting uranium product, referred to as 'OK liquor', then flows into the boildown circuit where it is concentrated into uranyl nitrate hexahydrate (UNH) by the evaporation of water and a small amount of nitric acid. In the final stage of the uranium refining process, uranyl nitrate hexyhydrate flows into the denitration area where it is thermally decomposed to form uranium trioxide [42].



Figure 3: General Overview of the Key Process at the BRR: Uranium ore concentrate (UOC) is digested in nitric acid and conditioned with phosphoric acid. This slurry passed through solvent extraction to produce OK liquor. As the OK liquor passes through the boildown circuit it becomes uranyl nitrate hydrate (UNH), which then passes through denitration to produce uranium trioxide as a final product [42].

As shown in Figure 4, the nitric acid recovery circuit includes the nitric acid absorbers, concentrators and rundown tanks. Resulting nitric oxide gases produced during the digestion and denitration processes flow to the nitric acid absorbers. Water and nitric acid evaporated from the raffinate are directed to one of the two nitric acid concentrators. As shown in Figure 5, nitric acid is also formed inside venturi scrubbers that also serve to condense water vapor in the gas streams exiting the digestors, denitration pots and the DRaff drum dryers and calciner. Denitration and digestion scrubber acid are fed directly to the digestion circuit, while DRaff scrubber acid is directed to the nitric acid rundown tanks [42].



Figure 4: General Nitric Acid Flow Summary: Nitric acid from the concentrators is pumped to the rundown tank. Nitric acid from the absorbers runs through the chloride removal circuit. Part of the treated nitric acid is pumped to solvent extraction circuit and part of it is pumped to the rundown tank. The absorber acid can also be pumped to the solvent extraction circuit prior to entering the chloride reactors. Nitric acid from the rundown tank is rerouted back to the first stage of digestion. Nitric acid from the denitration scrubber tank is pumped to the digestion circuit in order to utilize the acid and recover the uranium contained in the acid [42].



Figure 5: Denitration Scrubber Acid: There are 13 denitration pots in the denitration circuit. Each denitration pot has an off-gas chimney for NOx gas and water vapor removal. Cooled denitration scrubber acid from the denitration scrubber tank is pumped to each pot's venturi scrubber to condense the water vapor and convert a significant amount of NOx into nitric acid. The nitric acid formed inside the scrubbers flows back to the denitration scrubber separator tank along with the NOx fumes. The fumes are drawn from the separator tank to the absorbers via a Spencer turbine. Part of the liquid is recirculated to the pots with the remainder discharged to the digestion area to maintain a constant level inside the separator tank. Condensation of water vapor and absorption of NOx results in a constant nitric acid strength range between 47.0-50.0%; (due to the relatively constant water content of the UNH and the relatively constant efficiency of the venturi scrubbers) [42].

3.2.3 Chloride Circulation Profile

The average chloride concentration for 2009 in the slurry feeding the solvent extraction circuit was 675.0 mg Cl/L [43]. Recall that the solvent extraction circuit is comprised of three columns. The aqueous phase that exits the bottom of the extraction column contains the impurities from the UOCs that are not loaded onto the solvent along with most of the nitric acid and chlorides that were present in the slurry. This liquid is referred to as raffinate and it is pumped from the bottom of the extraction column into the raffinate holding tanks. Raffinate then flows through two evaporators, which boil off water along with nitrogen based and chloride based acids into the nitric acid concentrators [42].

As shown in Figure 6, NOx gases from D-Raff, scrap recovery, denitration and digestion flow to the Spencer turbine which then discharges the gases under pressure into the bottom of the lead nitric acid absorber. Both of the nitric acid absorbers consist of 20 internalized stainless steel bubble-cap trays inside vertical stainless steel columns. Process water or recycled condensate flows down from the top of the absorber A counter-current to the NOx gases from the Spencer turbines which enter through the bottom of absorber B. As the NOx gas rises through the trays it comes into contact with the process water and forms nitric acid. The additional NOx gas from absorber B is pumped to the bottom of absorber A where weaker nitric acid is formed. The nitric acid strength increases as process water flows to the bottom [42]. The average concentration of chlorides in the bottom of the absorber B in 2009 was 690.0mg Cl/L [43].

As shown in Figure 7, chlorides evaporated from the two raffinate evaporators flow into the nitric acid concentrator, where nitric acid gas is condensed and 'concentrated' while most of the water vapor exits the top of the distillation column.



Figure 6: Nitric Acid Absorbers: NOx gas from the Spencer turbine enters below the first tray in Absorber B. The NOx gas to the Spencer turbine inlet line comes from 4 circuits in the refinery: digestion/SX; scrap recovery; D-Raff; and denitration . There are 20 trays within each of the absorbers to convert the NOx gases into nitric acid. The circuit starts with process water or recycled condensate flowing down absorber A from tray to tray. Remaining NOx off-gas from absorber B is pumped below the first tray of absorber A. The nitric acid concentrated from absorber A is weak and is pumped to the top of absorber B. The weak acid comes into contact with concentrated NOx gas from the Spencer turbine as it drops down each tray. The result is strong nitric acid production out the bottom of absorber B. This is the sampled nitric acid since absorber B acid is the only absorber acid pumped to the chloride removal circuit [42].
As shown in Figure 7, corrosion problems, due to recirculating chloride, are most evident in the nitric acid concentrators. Chloride circulation in the nitric acid concentrators is cumulative due to the chemical properties of the chloride/water azeotrope. Chlorine gas reforms due to the increased nitric acid strength near the bottom of the concentrators [35]. Chlorine gas then rerises up the concentrator where it redissociates into chloride ions. This circulation profile causes chloride concentrations to increase and remain trapped within the concentrators. This is devastating for the corrosion of the 304-stainless steel in the concentrators. The average chloride concentration for concentrator acid in 2009 was 1004.0mg Cl/L [43]. The nitric acid concentrator consists of 12 stainless steel bubble cap trays inside a stainless steel column. Process water or recycled condensate flows down from the top of the concentrator, whereas vapors from the raffinate evaporators flows upward and enters below the first and fourth tray. As water flows down from tray to tray it is concentrated into nitric acid from condensing nitric acid vapors [42]. Chloride concentrations are typically high from the bottom of the concentrator up to the sixth tray due to the condensation/evaporation cycle of chloride compounds. Samples are taken from the nitric acid at the bottom of the concentrator, as well as trays 2, 4, 6, 8, 10 and 12. The higher concentrations are: 1000.0 mg Cl/L (bottom), 1220.0 mg Cl/L (tray 2), 1400.0 mg Cl/L (tray 4), and 850.0 mg Cl/L (tray 6) [43]. Chloride concentrations drop significantly above the eighth tray (185.0 mg Cl/L) due to the condensation of chloride compounds and their flow back down into the trays below [42].



Figure 7: Nitric Acid Concentrators: The nitric acid concentrators (A or B) receive water and nitric acid vapors from raffinate. There are two vapor inlet lines. The first enters below the first tray; (vapors higher in nitric acid from the second stage of evaporation) and the second one; (vapors low in nitric acid from the first stage evaporator) enters below the fourth tray for whichever concentrator is in operation. There are 12 trays that direct the flow of liquids down the concentrators. As nitric acid vapor rises it is preferentially condensed and joins the liquid flow; whereas, water preferentially evaporates from the tray and exits the top of the concentrator as a vapor. The condensed vapors

from the top of the concentrator flow to the barometric seal tank. Tail gases from the "A" absorber exit the refinery through the absorber stack [42].

3.2.4 Current Chloride Removal Circuit

As shown in Figure 8, the current chloride removal circuit at BRR consists of three main equipment packages: an ozone generator, three chloride reactors and an off-gas scrubber system. The ozone generator receives dry air from the chloride removal desiccant dryers that are fed from the powerhouse compressed air system. Ozone is produced in the ozone generator by passing dry air between high and low voltage electrodes (dielectric). When air passes through the electrical discharge between the two electrodes, some of the oxygen in the air is transformed into ozone. The ozone-rich air is fed to all three chloride reactors, which are operated in series. Untreated nitric acid is fed directly from the nitric acid absorber circulating pump to the top of the first chloride reactor. The nitric acid flows by gravity from the first reactor to the second reactor and subsequently to the third reactor. As the nitric acid flows through the chloride reactors it comes into contact with the ozone-rich air, which is injected through a venturi type mixing nozzle into the nitric acid recirculation pump located at the bottom of each reactor. The treated nitric acid from the third reactor is pumped to the nitric acid rundown tanks and a small amount is diverted to the solvent extraction circuit for acidification of the treated solvent [34].



Figure 8: Chloride Reactors: Nitric acid is pumped in from the bottom of nitric acid absorber B. The acid flows through three chloride reactors, which are set up in series. Ozone-rich air from the ozone generator is pumped into the recirculation pumps. The nitric acid inside the reactors is contacted by the ozone-rich air as it rises up through the columns. The gases that are formed by oxidizing chlorides, as well as NO_x , air and unused ozone bubble out of the reactors into the off-gas stream at the top of each reactor. These off-gases then flow to the caustic scrubbing system. The treated acid flows out of the third reactor where it then flows in two separate pathways: part of the nitric acid flows to the solvent extraction circuit and the rest flows to the nitric acid rundown tanks [34].

The tops of the chloride reactors are kept under slight negative pressure in order to draw all of the gases leaving the reactors into the scrubber system via the scrubber exhaust fan. The chloride ions are oxidized

to chlorinated gases, which flow into the off-gas caustic scrubber system for treatment. Other chloride reactor off-gases include: non-reacted ozone, nitric acid fumes, air (carrier gas) and oxides of nitrogen. As shown in Figure 9, the acidic off-gas is contacted with the alkaline scrubber solution leaving only trace amounts of chlorides, ozone and NOx gases. The off-gas then passes through two demisters for the removal of entrained liquids. Thereafter, the off-gas flows to the ozone destructor unit, which catalytically converts any remaining ozone back to oxygen. The scrubbed off-gas is then discharged to the absorber stack [34].



Figure 9: Chloride Removal Circuit Scrubbing System. The off-gases from the chloride reactors, which include NOx, chlorinated gases and ozone, flow into the wet scrubber. Ozone does not readily dissolve in the wet scrubber liquid so the off-gases (under slight negative pressure) from the scrubber flow through an ozone destructor prior to being emitted out the absorber stack. The wet scrubber is fed with water and sodium hydroxide to maintain a pH of 7 in the second stage scrubber tank. The pH of the overflowing scrubber liquid is about 1.4, which overflows from the first stage scrubber tank. The chlorinated gases readily dissolve as chloride ions in the scrubbing solution. Some of the NOx gas also dissolves into solution as nitrate or nitrite ions. The scrubber liquid overflows from the east side of the wet scrubber to the blowdown tank. It is pumped from there to the aeration tank. Hydrogen peroxide is added upstream to the aeration tank and air is added to the tank to convert the nitrite ions to nitrates before the tank overflows to the west neutralization tank where it is discharged to the lagoons for monitoring and discharge into Lake Huron [34].

Chloride assays in the nitric acid recovery circuit and chloride removal circuit are provided by the analytical department once per week. The average concentration of chlorides in absorber nitric acid for 2009 was 690.0mg/L [43]. The average concentration of chlorides in the treated nitric acid exiting the chloride removal circuit was 350.0mg/L in 2009 [43]. Therefore, the average chloride extraction efficiency of the current chloride removal circuit was 49.0% in 2009 [34].

It is important to note that the initial design of the current chloride removal circuit was intended to treat the nitric acid coming out of the concentrators. As previously mentioned, the chloride issue is a major concern for the nitric acid concentrators due to the chloride/chlorine transformational behavior in the acid. Chloride remains trapped in the concentrators. Concentrator nitric acid also contains a large amount of metallic impurities due to the fact that there is always a bit of entrainment of liquid raffinate as vapor that flows into the concentrator from the two raffinate evaporators. Recall that the impurities from the UOCs enter the solvent extraction column in the solvent extraction circuit and are drained to the raffinate. Raffinate has significant levels of metals such as: iron, molybdenum, nickel, cobalt, sodium and potassium that end up in the calcined product, but can be carried over into the concentrator nitric acid. If concentrator nitric acid were to flow through the chloride removal circuit it would foam due to the production of metallic salts. Also, the presence of impure metals in the concentrator acid attracts the ozone from the ozone-rich air. The metals become oxidized as opposed to the chloride in the acid, which drastically decreases the amount of chlorides being removed in the reactors [44].

3.2.5 Concerns Regarding the Current Chloride Removal System

The most pressing concerns regarding the chloride removal circuit are: energy requirements; repair and maintenance costs; and environmental effects. An internal study at the BRR performed by Jonathan Smith investigated the energy requirements for the chloride removal circuit [19]. It was discovered that the ozone generator required an average of 121.4 kW of power to operate. A conservative estimate of the average cost of electricity feeding the BRR is \$0.07/kWh. Therefore, the average cost for daily energy use in 2009 amount to [19]:

 $(121.4 \text{kW}) \ge (24 \text{ hours / day}) \ge (30.07 \text{/kWh}) = (203.95 \text{ per day})$

The BRR operated for 240 days in 2009. Therefore, in terms of annual energy requirements cost, the total amount required to run the ozone generator in 2009 was [19]:

 $($203.95 / \text{operating day}) \times (240 \text{ operating } \text{days} / \text{year}) = $48,984.00 \text{ per year}.$

There was also an investigation conducted to determine the energy requirement for the pumping system in the chloride removal circuit. The process units investigated for energy consumption were: the recirculation pump; nitric acid pump; blowdown pump; cooling water booster pump; scrubber recirculation pump; and the ozone destructor blow pump. In total, 89.2 kW of power was required to power the pumps in the chloride removal circuit. Therefore, the average cost for daily energy use in 2009 amounted to [19]:

 $(89.2 \text{kW}) \ge (24 \text{ hours / day}) \ge (0.07 \text{kWh}) = (0.07 \text{kW}) =$

As discussed previously, the BRR operated for 240 days in 2009. Therefore, the annual cost to run the pump system in the chloride removal circuit in 2009 amounted to [19]:

 $($149.85 / \text{operating day}) \times (240 \text{ operating days} / \text{year}) = $35 956.80 \text{ per year}.$

In total, which includes both the pumping system and the ozone generator, the current chloride removal circuit required a cost of \$84 940.80 in 2009 [19].

This total energy requirement is a major capital cost for operating an inconsistent chloride removal system. It is not cost-beneficial in terms of the amount of chloride being removed from the nitric acid circuit. The chloride removal circuit required the following amount of energy to operate in 2009 [19]:

 $(210.6 \text{kW}) \times (24 \text{ hours / day}) \times (240 \text{ operating days / year}) = 1.2 \times 10^6 \text{ kW per year}.$

In terms of carbon dioxide emissions related to the power retrieved from the Ontario Power Grid, the total for 2009 was 4.55×10^5 kg of carbon dioxide (see section 4.3.2 for calculations).

Another concern regarding the chloride removal circuit is the cost associated with the continuous repairs and maintenance required to the circuit. According to an internal inquiry provided by Rosanna Rainville (2010), the total cost for repairs and maintenance in 2009 was \$39 984.02 [21]. The most common issues that required repairs and maintenance were repairing acid leaks in the chloride reactors, as well as replacing leaky gaskets in the ozone generator, chloride reactors and the off-gas valves [21]. The total repair and maintenance costs associated with the chloride removal circuit are high in terms of the efficiency in which it removes chloride from the nitric acid stream.

The nitric acid recovery circuit repairs and maintenance costs for 2009 were also considered. Corrosion of stainless steel pipes, vessels and gaskets is a major cost issue for the BRR. The total annual cost in 2009 for repairs and maintenance to the nitric acid recovery circuit was \$229,496.16 [22]. A substantial amount of the total costs was due to corrosion issues in the circuit.

The major environmental concerns identified in the chloride removal circuit are: potential loss of ozone to the external environment via the absorber stack; excessively high concentrations of nitrites in the scrubber blowdown; high concentrations of NOx exiting out the absorber stack; a potential loss of nitric acid to groundwater; and potential contamination of the process effluent [34].

The loss of ozone to the atmosphere through the absorber stack can be caused by improper valve arrangements or leaky valves or ineffective ozone destruction. Elevated concentrations of chlorine in the reactors (above the liquid) and in the piping renders the stainless steel more susceptible to corrosion and increases the likelihood of structural damages to the piping systems, valves and gaskets. This significantly increases the chances of having ozone leaked into the work environment and the atmosphere. If the ozone destruction unit was working inefficiently or bypassed, if there was a leak in the stainless steel exhaust piping to the scrubbers, or the ozone lines between the generator and the reactors then elevated levels of ozone would escape into the atmosphere. Operator training and surveillance and replacement of the catalyst on a regular basis are precautionary measures that have been put in place [34].

Ground level ozone can pose dangerous health and environmental effects at elevated concentrations. Breathing ozone into the body can trigger a variety of health problems which include: chest pain, coughing, throat irritation, and congestion. The intake of ozone has also been shown to increase the effects of bronchitis, emphysema, and asthma. Ground-level ozone lowers the functionality of the lungs and causes inflammation in the linings of the lungs. Ground level ozone also has dangerous effects on the local environment and ecosystems. Elevated concentrations of ozone have been shown to interfere with the ability of certain plants to produce and store nutrients. Ozone also damages leafs and branches of nearby trees due to its oxidative properties and decreases plant growth and reproduction. The destruction of plants and leaves reduces the ability of vegetation to undergo photosynthesis and ultimately reduces the amount of carbon dioxide that is eliminated from the atmosphere [45].

NOx and nitrite emissions are also important health and environmental concerns at the BRR. Elevated concentrations of NOx and nitrites can pose dangerous health threats. One of the most serious health threats is acute acquired methemoglobinemia. Under normal physiological conditions, hemoglobin molecules contain iron within a porphyrin heme structure. The iron in hemoglobin molecule is normally

found in the Fe^{2+} state. The danger of nitrites and NOx is that the iron moiety of hemoglobin can be oxidized to the Fe^{3+} state to form methemoglobin. Once methemoblobin is formed, the red blood cell component loses its ability to carry molecular oxygen. This leads to hypoxia and can be lethal if the exposure persists [11]. NOx emissions in the atmosphere are dangerous for the environment for many reasons: they catalyze ground-level ozone formation; they are a component of smog; they contribute to the production of acid rain; they are greenhouse gases (N₂O) that contribute to global warming and climate change; and they reduce oxygen levels in local water sources [45]. These issues will be further discussed in section 4.3 since they are a concern for both the current and proposed alternative chloride removal systems.

3.3 Consideration of Alternative Methods for Chloride Removal

The alternatives for a new chloride removal system were drawn upon the principle of oxidizing chloride ions in nitric acid to chlorine gas. There are six alternative options provided in this research. As shown in Figure 10, each alternative incorporates bleeding denitration scrubber acid into the absorber acid:



Figure 10: Absorber and Denitration Nitric Acid Blend: All six alternatives propose that denitration scrubber acid should be bled into the absorber nitric acid prior to flowing through the first chloride reactor. The 304-stainless steel line would be connected downstream of the scrubber automatic level control valves and would direct denitration scrubber acid to the first chloride reactor where it would join "fresh absorber nitric acid" and premixed acid inside the reactor. Bleeding the denitration nitric acid into the absorber nitric acid at this location is crucial for quickly elevating the nitric acid strength and allowing the release of chlorine gasinside a vessel that is designed to handle this corrosive gas. It also prevents chlorine gas from forming in the absorber lines prior to entering the chloride reactors.

Alternative 1: Blend the absorber and denitration scrubber acid with a volumetric ratio that obtains a minimum of 43.0% nitric acid strength without any gas flow through the eductor pumps in the chloride reactors (see Figure 10). This alternative is based on the principle that sufficient amounts of chlorides will be oxidized to chlorine gas based on the strength of the acid alone. 43.0% nitric acid is strong enough to naturally produce sufficient amounts of NOx gas (fuming nitric acid), such as nitrous oxide, which could oxidize the chloride ions into chlorine gas.

Alternative 2: Blend the absorber and denitration scrubber acid with a volumetric ratio that obtains a minimum of 43.0% nitric acid strength. After the nitric acids have been blended they would be sparged

with air from the powerhouse (see Figure 11). The air would be pumped into the eductor pumps where ozone-rich air is currently being injected. This principle draws upon the same principle as alternative 1, except the addition of air to the solution provides a path to allow entrained gases to leave the acid and fluid agitation to further oxidize the chlorides from the solution. Oxygen will also provide additional oxidation of chloride ions in solution due to the fact that its ORP value will likely be higher than that of chlorine at 43.0% nitric acid.

Alternative 3: Blend the absorber and denitration scrubber acid with a volumetric ratio that obtains a minimum of 43.0% nitric acid strength and purge the solution with NOx gas from the Spencer turbine (see Figure 12). Again, this principle draws upon the same principle as alternatives 1 and 2, except the addition of NOx to the solution provides stronger oxidants (nitric oxide and nitrous oxide) than oxygen to further oxidize the chlorides from the solution.

Alternative 4: Blend the absorber and denitration scrubber acid with a volumetric ratio that obtains a minimum of 43.0% nitric acid strength. Thereafter, the blended nitric acid would be sparged with a combination of both plant air from the powerhouse and NOx gas from the Spencer turbine (see Figures 11 and 12). The gas lines into the bottom of the chloride reactors would be a blend of plant air and NOx.

Alternative 5: Blend the absorber and denitration scrubber acid with a volumetric ratio that obtains a minimum of 43.0% nitric acid strength. The blended nitric acid would then be sparged with plant air (see Figure 11). In addition to sparging with air, the ozone generator would be run periodically to flush out additional chloride.



Figure 11: Dry Air SpargingCircuit: Alternatives 2, 4 and 5 would require external air to be compressed in the powerhouse and discharged to the chloride reactors. The air would be sparged into the blended nitric acid through the eductor pumps at the bottom of each chloride reactor. The air would pass through the same lines that are currently being used to inject ozone-rich air. The only difference is that the ozone generator would be shut down and only air would flow to the reactors.

Alternative 6: Blend the absorber and denitration scrubber acid with a volumetric ratio that obtains a minimum of 43.0% nitric acid strength and purge with ozone based on the current chloride removal circuit.



Figure 12: NOx Sparging Circuit: Alternatives 3 and 4 would require that a NOx gas line be installed from the Spencer turbine to the chloride reactors. The NOx lines would run where the ozone-rich air lines are currently installed. NOx would be sparged into the eductor pumps at the bottom of the chloride reactors.

The idea for alternative 4 is to accommodate for the concerns of the first three alternatives. Alternatives 1 and 2 may not provide enough oxidation to remove sufficient amounts of chlorides. Alternative 3 may produce too many negative environmental impacts associated with additional NOx gas being emitted out the absorber stack and additional nitrites being emitted in the plant effluent. Therefore, alternative 4 may potentially provide the balance between efficient chloride removal, costs and environmental impacts. Alternative 5 is similar to alternative 2, except that periodic sparging with ozone periodically will be beneficial since the level of chloride extraction using ozone would drastically increase with stronger nitric acid passing through the chloride reactors. Alternative 6 is the same circuit that is currently being used with the exception that stronger nitric acid would be flowing through the chloride reactors as a result of the blend.

3.4 Data Collection Methods

3.4.1 Refinery Sample Collection

The primary method for collecting data for this research was daily sampling of nitric acid from the bottom of absorber B and the bottom of the denitration scrubber tank. In the nitric acid recovery circuit, there is a sample station that has been put in place to easily sample all nitric acid streams. There is a sink containing sampling pipes coming from the nitric acid concentrators, absorbers, rundown tanks and denitration scrubber tanks [42]. For this thesis, only nitric acid from absorber B and denitration scrubber A was sampled, since they had proven to provide the most consistent data in the past. Also, these are the only two sample points that were sampled, since they are the two acid streams that are targeted for blending. Denitration scrubber A and B are very similar in terms of chloride concentration and nitric acid strength; therefore, either of the two could have been sampled.

A daily sample of 100.0mL of nitric acid was taken from the bottom of the nitric acid absorber, which is located in the nitric acid recovery circuit, for 60 operating days. 100.0mL of denitration scrubber acid was also sampled daily for 60 operating days. Although the denitration scrubber tanks are not located in the nitric acid recovery circuit, denitration scrubber acid was used as a source of strong nitric acid (50%) with a negligible concentration of chloride (<50 mg/L). Varying ratios of absorber and denitration scrubber acid were blended in order to produce a nitric acid strength scale ranging between 36-50%. The blended ratios of absorber to denitration nitric acid were: 3:1; 2:1; 1:1; 1:2; and 1:3. There were seven samples prepared prior to laboratory tests as shown in Table 3:

Blend Number	Volume of Absorber	Volume of Denitration	Total Volume (mL)
	Nitric Acid (mL)	Scrubber Acid (mL)	
1	20.0	—	20.0
2	_	20.0	20.0
3	15.0	5.0	20.0
4	13.3	6.7	20.0
5	10.0	10.0	20.0
6	6.7	13.3	20.0
7	5.0	15.0	20.0

Table 3: Blended Nitric Acid Sample Preparation for Laboratory Analysis

3.4.2 Laboratory Data Collection from Refinery Samples

The first laboratory test conducted was a free acid test to determine the acid strength of the absorber and denitration nitric acids. The analytical procedure for this test was provided in BRR:CAM:FA:7 [40]. In summary, 200.0 μ L of nitric acid was added to 50.0mL of potassium oxalate. The potassium oxalate was prepared to have a pH of 6.05. Once the 200.0 μ L of nitric acid was added to the potassium oxalate, the next step was the addition of sodium hydroxide in order to lower the pH back to 6.05. A digital pH reader was provided to read the sample. The volume of sodium hydroxide added was monitored and used in the calculation. There was a standard titration chart provided in the laboratory with 0.2mL increments that associated the sodium hydroxide titration volume with the corresponding acid strength. The confidence level for this test is 95% according to the analytical procedure [40].

Once the nitric acid strengths had been determined, the next step was the preparation of samples for the UV-visible spectrometer [38]. The first three samples prepared served as the blank, high and low standards. The high and low standards (samples 2 and 3) were prepared using a standard chloride solution, which included sodium chloride and ultra-pure water. Ammonium sulphate was added to the solution, since it is an inorganic salt used to bind calcium cations. Calcium's cations interfere with the UV-visible spectrometer readings, since they absorb UV light in the 460nm range. Mercuric thiocyanate was also added to each solution. Mercuric thiocyanate reacts with iron chloride to form the secondary compound Fe(SCN)²⁺. This compound was used to measure the concentration of chloride, since it was formed as a result of the extent of the reaction between chloride ions and mercury thiocyanate as an equivalency [38]. An aliquot of each sample (i.e., the volume of nitric acid from the 20.0ml samples shown in Table 3) was added to a 30.0mL beaker. A smaller volume of aliquot was added to solutions with higher anticipated chloride concentrations in order to maintain accuracy of UV light absorption. Table 4 summarizes the preparation of samples for the UV-visible spectrometer:

Sample	Absorber	Denitration	540 ppm	125 ppm	Ultra-	Mercuric	Ammonium
Number	Nitric Acid	Scrubber	Chloride	Chloride	Pure	Thiocyanate	Sulphate
	(mL)	Nitric Acid	Standard	Standard	Water	(mL)	(mL)
		(mL)	Solution	Solution	(mL)		
			(mL)	(mL)			
1					28.0	1.0	1.0
2			1.0		27.0	1.0	1.0
3				1.0	27.0	1.0	1.0
4	0.2				27.8	1.0	1.0
5		1.0			27.0	1.0	1.0
6	0	.5			27.5	1.0	1.0
7	0.5				27.5	1.0	1.0
8	0.5				27.5	1.0	1.0
9	0	.5			27.5	1.0	1.0
10	0	.5			27.5	1.0	1.0

 Table 4: Sample Preparation for the UV-Visible Spectrometer.
 Samples 6-10 represent the blended nitric acid solutions shown in Table 3 (3:1; 2:1; 1:1; 1:2; and 1:3 blend ratios of absorber to denitration nitric acid).

It is important to note that samples 5-10 were blended without being sparged with air. This was used to test the efficiency of alternative 1. Once samples 1-10 had been prepared, the 200.0mL beakers containing 20.0mL of blended acid were sparged with dry air for 1 minute. This provided the data required to determine the efficiency of alternative 2. The compressed air was sparged from an air pump in the laboratory through a plastic tube inserted into the solution. The goal was to mimic the effect of sparging the acid with plant air. Sparging the solutions for 1 minute was conducted in order to demonstrate if chlorides can be oxidized by oxygen present in the plant air or if entrained gases can be removed from the acid. In future test work at the refinery, the "sparging effect" can be scaled up to the actual residence time of the nitric acid in the chloride reactors. Once the solutions had been sparged with air they were prepared as samples 11-15 for analysis using the UV-visible spectrometer. Each sample contained the same components as samples 6-10; (i.e. 27.5mL of ultra-pure water + 0.5mL of blended acid + 1.0mL mercuric thiocyanate + 1.0mL ammonium sulphate).

Sample 16 was set up to purge NOx gas through a blended acid ratio of 1:1 denitration scrubber acid to absorber acid. The 1:1 ratio was the only ratio tested, since this was the most realistic scenario for this alternative (based on available denitration scrubber acid to use for the blend and due to operational and

safety concerns associated with the test procedure). This will be further discussed in section 4.4. The ratios would have been modified if the results of the tests did not provide the expected reduction in chloride concentrations. A special container was constructed in the BRR maintenance shop to be able to sparge NOx through the nitric acid samples, as shown in Figure 13:



Figure 13: **NOx Sparge Container:** The NOx sparging location is situated within the refinery near the Spencer turbines. There are two NOx gas lines running through this area. The first line originating on the turbine's outlet is under positive pressure and the second line originating on the turbine's inlet is under negative pressure. There are two block valves in each of the two sample lines.

The NOx sparge container was constructed out of 304-stainless steel. The total volume of nitric acid poured into the NOx container was 1000.0mL with a denitration scrubber acid to absorber acid volumetric ratio of 1:1. This was accomplished by adding 500.0mL of denitration scrubber acid and 500.0mL of absorber B acid. The blended nitric acid was poured and sealed in the NOx sparge container and then sparged with NOx gas for 30.0 seconds. The nitric acid was then brought back to the laboratory and read

on the UV-visible spectrometer along with samples 1-15. Samples 16 and 17 were set up to test alternatives 3 and 4 respectively. Nitric acid acquired from sparging NOx through a 1:1 blend was sparged for one minute with dry air for sample 17. Samples 16 and 17 were set up for the UV-visible spectrometer the same way as samples 6-11, as shown in Table 5:

Sample Number	Air Sparge		NOx Sparge	
	Pressure (psi)	Duration (sec)	Pressure (psi)	Duration (sec)
11	4.0	60.0	—	—
12	4.0	60.0	—	—
13	4.0	60.0	15.0	30.0
14	4.0	60.0	—	—
15	4.0	60.0	—	—
16	—	—	15.0	30.0
17	4.0	60.0	15.0	30.0

Table 5: Preparation of Samples 11-17 (Sparging Procedure for Blended Nitric Acid Solutions)

Once the 17 samples had been prepared for the UV-visible spectrometer, the final step was the measurement of UV absorbance. The general operation of the UV-visible spectrometer is provided in the analytical procedure BRR:CAM:GEN:66 (2009) [38]. Each sample was put into a UV sample vial and inserted into the spectrometer. The wavelength that was used for the absorbance readings for this method was 460.0nm [38]. The blank was run first and the instrument was zeroed in order to accurately measure the chloride concentration without any bias from the ultra-pure water. Each sample was run thereafter and the absorbance value was used to calculate the chloride concentration. There was a UV absorbance chart in the laboratory that was used to determine the chloride concentrations in the various nitric acid samples. Section 3.5.1 will demonstrate how the chloride concentration was calculated using these procedures.

3.4.3 Administrative and Environmental Emissions Data Collection

Administrative and environmental emissions data for this research was acquired by retrieving analytical data input on the AS 400 system and process flow diagrams from the BRR facility radiation officer, environmental coordinator, chief process engineer, and administration department. The following data was acquired from the AS 400 for the year 2009: chloride concentration in absorber acid; chloride concentration in ozone treated acid; chloride in denitration scrubber acid; chloride in uranium ore concentrate; chloride in slurry; chloride in OK liquor; chloride in the barometric seal tank; chloride in raw well water; chloride in raffinate/calcined product; chloride in the

aeration tank; chloride concentration in effluent discharge; nitrite concentration as nitrogen in effluent discharge; uranium concentration in the blowdown tank; uranium concentration in effluent discharge; NOx atmospheric emissions out the absorber stack; pH of effluent discharge; and uranium concentration in denitration scrubber acid. Process flow diagrams were acquired to analyze the flow rates of various liquids and gases. This information provided the data necessary to calculate the chloride and nitric acid mass balances. In addition to AS 400 data collection, annual costs for 2009 regarding the chloride removal circuit and the nitric acid recovery circuit were acquired from the administration department.

3.5 Data Analysis Methods

3.5.1 Level of Chloride Extraction Comparisons

A standard nitric acid strength versus chloride concentration curve was constructed in order to provide a baseline graph for the research. This was compared to the results obtained by Pierce et al. (2007). A standard solution of 30.0% nitric acid with a chloride concentration of 1000.0mg/L was prepared in the analytical lab. 70.0% pure nitric acid was added to 30.0% nitric acid at specific volumes in order to strengthen the nitric acid by 1.0%. This procedure was performed 18 times in order to produce a standard scale of nitric acid strengths from 30.0 - 48.0%. This scale represents the absolute minimum and maximum nitric acid strengths that can potentially flow through the chloride reactors. The standard test also provided information on the level of chloride oxidation resulting from nitrous acid gases (see Section 2.3.3), since there were not any nitric or nitrous oxide dissolved in the acid.

The theoretical chloride concentration of each blended nitric acid solution was calculated based on the volumes of 30.0% and 70.0% nitric acid. The volumetric ratio of 30.0% nitric acid and 70.0% nitric acid used to produce the desired nitric acid strength was calculated according to the following algebraic method:

$$(X) (0.30) + (20-X) (0.70) = (Y) (20)$$
(14)

Where X is the volume of 30.0% nitric acid added to a total volume of 20.0mL and Y is the desired nitric acid strength percentage. The volume of 70.0% nitric acid to add to a total volume of 20.0mL was

calculated via 1-X. For example, in order to obtain 31.0% nitric acid the following volumes of 30.0% and 70.0% nitric acid must be blended:

(X) (0.30) + (20-X) (0.70) = (0.31) (20); 0.30X + 14 - 0.70X = 6.2; 0.70X - 0.30X = 14 - 6.2; 0.40X = 7.8; X = 7.8/.040; X = 19.5 (volume of 30% nitric acid in mL) and 1- X = 0.5 (volume of 70% nitric acid in mL)

Total Nitric Acid	Theoretical	Volume of 30%	Volume of 70%	Total Volume
Strength	Chloride	Nitric Acid (mL)	Nitric Acid (mL)	(mL)
(%HNO ₃)	Concentration			
	(mg/L)			
30	1000	20.0	0.0	20.0
31	975	19.5	0.5	20.0
32	950	19.0	1.0	20.0
33	925	18.5	1.5	20.0
34	900	18.0	2.0	20.0
35	875	17.5	2.5	20.0
36	850	17.0	3.0	20.0
37	825	16.5	3.5	20.0
38	800	16.0	4.0	20.0
39	775	15.5	4.5	20.0
40	750	15.0	5.0	20.0
41	725	14.5	5.5	20.0
42	700	14.0	6.0	20.0
43	675	13.5	6.5	20.0
44	650	13.0	7.0	20.0
45	625	12.5	7.5	20.0
46	600	12.0	8.0	20.0
47	575	11.5	8.5	20.0
48	550	11.0	9.0	20.0

 Table 6: Theoretical Nitric Acid Strengths vs. Chloride Concentrations: This table displays the theoretical chloride concentrations associated with the various acid blends. The blended acids were set up to create a nitric acid strength scale versus chloride concentration.

The actual chloride concentrations were analyzed based on the readings from the UV-visible spectrometer. These chloride concentrations were then compared to the theoretical chloride concentrations in order to determine the level of chloride extraction as a result of nitric acid strength (i.e. resulting from nitrous acid fumes).

This standard test involved preparing a 1.0L stock solution of 30.0% nitric acid with a chloride concentration of 1000.0mg/L. In order to prepare this solution, the amount of 70.0% pure nitric acid, ultra-pure water and sodium chloride to add was first determined. The following steps were used to determine the relative amount of components to add to a total volume of 1.0L:

• To obtain 30% nitric acid the following ratio of 70% pure nitric acid to ultra-pure water must be mixed:

(0.70)(X) = (0.30)(1000)

0.70X = 300

X = 430

Therefore, 430.0mL of 70.0% pure nitric acid was blended with 570.0mL of ultra-pure water in order to obtain 1L of 30.0% nitric acid.

• Sodium Chloride: The molecular weight of sodium chloride is 58.5g/mol. The molecular weight of chlorine is 35.5g/mol. In terms of chlorine composition in sodium chloride:

 $(35.5g/mol / 58.5g/mol) \ge 100\% = 60\%$

Therefore, 60% of sodium chloride is composed of chlorine. In order to obtain 1000mg/L the total amount of sodium chloride added was:

(1.0 L / 0.6) = 1.67 g

The theoretical chloride concentration was calculated based on the volumetric ratio of 30.0% to 70.0% nitric acid. Recall that pure 70.0% nitric acid does not contain any chlorides. The theoretical chloride concentration assumes that no chlorides are oxidized to chlorine gas and purged out of the 30.0% nitric acid solution. This baseline was used to determine the level of chloride extraction at various nitric acid strengths. For example, 40.0% nitric acid would have the following theoretical chloride concentration:

- 15mL of 30% nitric acid (75% of the total volume); and
- 5mL of 70% nitric acid (25% of the total volume)

Therefore,

[(0.75) (1000 mg/L Cl)] + [(0.25) (0.0 mg/L)] = 750 mg/L Cl

Field sample data was collected (as described in sections 3.4.1 and 3.4.2) and analyzed in an effort to test alternative chloride removal system recommendations from the list provided in section 3.3.

As discussed in section 3.4.2, chloride concentrations were determined by using a UV-visible spectrometer. In order to calculate the chloride concentration, the absorbance reading from the Cary 100 UV-visible spectrometer was converted using the following equation [38]:

$$[Cl] = [UV Absorbance x 25] / Aliquot$$
(15)

The aliquot is the volume of the sample that was used in the preparation. For the absorber acid, a 0.20mL aliquot was used, since the concentration of chloride is generally high and a higher aliquot would not have been able to be read within the UV-visible spectrometer wavelength range. The aliquot for the denitration scrubber acid was 1.0mL, since the chloride concentration was generally very low. The aliquot that was used for the three blended nitric acids was 0.50mL each. The absorbance reading from the UV-visible spectrometer has an associated chloride curve value that was plugged into the equation above.

3.5.2 Cost Comparisons

Data from 2009 was analyzed in order to demonstrate the high cost of operating the existing chloride removal circuit. The existing level of chloride extraction was compared with the overall maintenance and repair costs associated with the ozone generator and corrosion problems in the nitric acid and chloride removal circuits. Another major cost that was analyzed was the energy consumption required to power the existing chloride removal circuit. The existing circuit requires energy for several pumping systems, the main refinery air compressor and the ozone generator itself. The cost of the proposed alternative chloride removal circuits was analyzed in order to generate a cost comparison. The main cost data that was used for the alternative chloride removal circuits were: energy costs for the air compressor; costs of new piping to be installed and the cost of any additional nitric acid pumps that may be required.

3.5.3 Environmental Impacts Comparisons

Data from 2009 was used to analyze emissions associated with the existing chloride removal circuit. Relative carbon dioxide emissions from energy input from the provincial power grid were also calculated in order to evaluate the indirect environmental impacts generated by the existing chloride removal circuit power demands. Relative carbon dioxide emissions from energy input from the provincial power grid was then calculated for each alternative chloride removal circuit proposed in order to provide an emission comparison. Emissions associated with the chloride removal circuit are composed of NOx and ozone gases exiting the absorber stack, as well as nitrates and nitrites discharged in the plant effluent. A relative comparison between the current and alternative chloride removal circuits was generated for these parameters.

3.5.4 Operational Impact Comparisons

Data from test work and data available from refinery operating records was analyzed to determine the potential operational impacts that an alternative chloride removal circuit may have on the uranium refining process. The key operational impact areas associated with the alternative chloride removal system were: effects on the nitric acid mass balance; the denitration process; the solvent extraction process product quality: and uranium losses. All of these operational impacts will be addressed when evaluating if the alternative chloride removal circuits will be beneficial for the overall operation at the BRR.

4.0 Results and Discussion

4.1 Levels of Chloride Extraction

4.1.1 Current Chloride Removal Circuit Chloride Extraction



Figure 14: Absorber B Nitric Acid Strength Vs. Chloride Extraction: The data used for this figure was taken from January 2009 until April 2010. The nitric acid strength corresponds to the strength of the acid exiting the bottom of absorber B and passing through the chloride reactors. This data is intended to draw a correlation between nitric acid strength and level of chloride extraction. The value for each of the nitric acid strengths is an average over the 16-month period. The Y bar error represents the potential range of values based on the confidence level of the analysis (90% confidence level) [39].

Based on the results of Figure 14, there is an important threshold at 40.0 - 41.0% nitric acid strength where the level of chloride extraction increased from 52.0% up to 58.0%. Chloride concentrations in the absorber B acid were extremely low due to the evaporation of chloride inside the absorber tank. Although the level of chloride extraction was higher for nitric acid strengths between 41.0% and 42.0%, the average chloride concentration entering the chloride reactors from the absorber line was very low. This indicated a large amount of natural chloride oxidation to chlorine inside the absorber tank. Also, the level of chloride oxidation was much higher (above 70.0%) when the absorber B nitric acid chloride concentration was

higher going through removal circuit. The highest chloride concentrations occur in nitric acid below 37.0%, which indicates that the majority of the chlorides are being flushed out of the absorber. The trend for ozone effectiveness with acid strength would be expected to be a gradual rise such as that seen between 33.5% acid and 41.5% nitric acid strength.

An interesting consideration for 41.0 - 42.0% nitric acid strength was the relative amount of oxidation due to ozone and the relative amount of oxidation due to NOx fuming out of the acid. For the data presented above, temperature and fluid motion can be neglected due to the fact that they remain fairly constant throughout the range of nitric acid strengths. However, they do play an important role in producing NOx fumes out of the nitric acid. If ozone were to play a big role in the efficient chloride extraction it would be due to the destabilization of electrochemical bonds that causes an increase in oxidation rate. Recall that destabilization increases due to an increased concentration of positive hydrogen ions in the solution. This decreases the strength in electron orbit around the nucleus and renders the loss of electron(s) easier [35].

Perhaps efficient chloride removal at 41.0 - 42.0% nitric acid was also due to the effect of NOx and oxygen at 41.0 - 42.0% nitric acid strength. Not only does a greater concentration of positive hydrogen ions increase the rate of oxidation for ozone, it also increases the relative ORP of NOx and oxygen compared to chlorine. Recall from the literature review that the ORP of oxygen is slightly below that of chlorine at 1.0 M nitric acid strength. However, as nitric acid strength increased so did the relative ORPs of oxygen and NOx gases compared to chlorine. At 41.0 - 42.0% nitric acid strength the ORP value of oxygen would be well above 1.360V (chlorine) and would serve as an oxidant. Also, as discussed in Section 2.3.3, the ORP values of nitric and nitrous oxide are above that of chlorine at 1.0 M nitric acid strength and nitrous oxide are above that of chlorine at 1.0 M nitric acid strength. Therefore, in 41.0 - 42.0% nitric acid their respective ORPs would be significantly higher than 1.360V (chlorine). As a result, any NOx fumes emitted from the nitric acid containing nitric and nitrous acid would provide a source of chloride extraction (oxidation).



Figure 15: Absorber B Nitric Acid Strength Vs. Absorber Acid Chloride Concentration: The data used for this figure was taken from January 2009 until April 2010. The value for each of the absorber B nitric acid strengths is an average over the 16 month period. The threshold for maintaining chloride ions in the nitric acid solution is around 37.0% nitric acid. Nitric acid strengths above this threshold will cause significant amounts of chloride ions to oxidize to chlorine gas and recirculate through the absorber tank and cause corrosion damage. This will also reduce the potential to have a very high level of chloride extraction. The Y bar error represents the potential range of values based on two standard deviations. As shown in this Figure, there were fewer sample points (below 10) for nitric acids above 42.0%.

Based on the results of Figure 15, the most efficient operating range would be 37.0% nitric acid exiting the bottom of Absorber B, since the majority of chloride would still exist in ionic form (i.e., chloride ions would be flushed out of the absorber tank without being oxidized to chlorine gas naturally inside the tank). Maintaining the nitric acid strength at 37.0%, as opposed to 35.0 - 36.0%, would also reduce the volume of denitration scrubber acid required to increase the acid strength to 43.0% entering the chloride reactors. Absorber nitric acid strengths above 37.0% would also cause a significant amount of chloride to be oxidized to chlorine and remain trapped in the absorber tank, which would result in higher corrosion rates inside the absorbers. During the chloride extraction process the goal would be to increase the nitric acid strength from 37.0% to 42.0 - 43.0% prior to when the acid enters the chloride reactors by blending in nitric acid from the denitration scrubber tank. The increase in acid strength could potentially increase

the level of chloride extraction above 90.0% from increasing the nitric acid strength with the current chloride removal circuit (i.e., sparging the acid with ozone).

As previously discussed by Wilkinson (1961), the use of ozone generation as a means to oxidize chloride in nitric acid has several problems: high maintenance costs; high capital costs for operation; and inconsistent chloride oxidation [31]. This case is true for the use of ozone in nitric acid below 40.0%. However, there is much greater potential for efficient chloride removal using ozone when the strength of nitric acid is around 42.0 - 43.0%. As discussed in Section 2.3, ozone is a stronger oxidant than oxygen, nitric oxide and nitrous oxide. Although ozone use has been inefficient when nitric acid strengths have been below 40.0%, it can potentially extract more than 95.0% of chloride present in 42.0 - 43.0% nitric acid, which is highly efficient.

In order to increase the nitric acid strength from 37.0% to 42.0 - 43.0% a volumetric ratio of approximately 1:1 absorber to denitration acid would have to be blended. Essentially all of the available denitration scrubber acid would have to be pumped to this blend point in order to accomplish this efficiency range. This ratio is based on the results from the 1:1 blended nitric acid strength tested in the laboratory during the entire research. The flow rates were determined by analyzing the process flow diagram for the nitric acid recovery and denitration areas. This will be further discussed in section 4.4.

4.1.2 Standard Lab Test: Chloride Extraction

As described in Section 3.5.1 and shown in Table 7, a standard lab test was performed on June 8, 2010. Although the nitric acid used in the standard lab test was different in composition than the refinery nitric acid, the purpose was to generate data for theoretical comparisons to the results obtained by Pierce et al. (2007).

Total Nitric Acid Strength (%HNO ₃)	Blended Acid Chloride Concentration (mg/L)	Blended Acid + Dry Air Purge Chloride Concentrations (mg/L)	Volume of 30% Nitric Acid (mL)	Volume of 70% Nitric Acid (mL)
30	1040	760	20.0	0.0
31.3	990	710	19.5	0.5
32.6	990	710	19.0	1.0
33.9	965	680	18.5	1.5

35.2	945	660	18.0	2.0
36.5	930	650	17.5	2.5
37.8	890	640	17.0	3.0
39.1	875	640	16.5	3.5
40.4	845	640	16.0	4.0
41.7	760	640	15.5	4.5
43.0	760	635	15.0	5.0
44.3	750	630	14.5	5.5
45.6	710	600	14.0	6.0
46.9	680	560	13.5	6.5
48.2	670	540	13.0	7.0

Table 7: Standard Lab Test: Nitric Acid Strengths vs. Chloride Concentrations: The anticipated 1.0% nitric acid strength increase per 0.50mL of 70.0% pure nitric acid added did not occur due to inconsistencies in the preparation methods. Also, the concentration of chloride in the 30.0% standard nitric acid solution was 40.0mg/L higher (1040.0mg/L instead of the predicted 1000.0mg/L). The strength of the nitric acid increased incrementally by 1.3%. Therefore, the scale was narrowed down from the original nitric acid strengths scale and included only nitric acid strengths within the possible operating range in the chloride reactors. Once chloride concentrations readings were done for each sample, dry air was then sparged through each solution for 1 minute at 4psi. A second round of chloride readings were then prepared (see Figure 16 for the results).

There was no chloride extraction observed during the standard lab test when the solution was not sparged with dry air. As discussed previously, nitric acid strength plays a catalyst role in terms of available hydrogen ions for the oxidation reaction. Pure nitric acid emits nitric acid (HNO_3) and nitrous acid (HNO_2) fumes. The ORP of nitric acid fumes is far too low to serve as an oxidiant of chloride ions. However, nitrous acid fumes would likely serve as a strong enough oxidant to oxidize chloride ions. Based on the results of the standard lab test, there were insufficient amounts of nitrous acid fumes produced to oxidize chloride ions in solution.

When each nitric acid solution was sparged with dry air for 1.0 minute at 4.0psi there was a noticeable amount of chloride oxidation that occurred. Since oxidation from nitrous acid fumes was ruled out from the first round of tests, the results of sparging the solution with dry air indicated that the ORP value of oxygen was high enough to oxidize a significant amount of chloride ions in nitric acid. The results of the standard lab test are presented in Figure 16.

The results of the standard lab test were used for comparing chloride extraction levels at low temperatures (i.e., below 30° C) with the results obtained by Pierce et al. (2007). As discussed by Pierce et al. (2007),

they did not observe any significant level of chloride extraction as the acid strength increased [33]. Similarly, the results obtained during this standard lab test (shown in Figure 16) revealed that there was no significant chloride extraction associated with nitric acid strength of pure nitric acid (without air sparging). As discussed previously, the lack of chloride extraction can be attributed to the absence of nitrous acid fumes produced from the solution. Pierce et al. (2007) did not provide a discussion regarding chloride oxidation from nitrous acid fumes; therefore, the results of the standard lab test were able to provide additional discussion for this observation.



Figure 16: Nitric Acid Strength Vs. Chloride Concentration (Blend / Blend + Dry Air). The Y bar error represents the potential range of values based on the confidence level of the analysis (90% confidence level) [36].

The standard lab scale test for nitric acid strength versus chloride concentration was conducted in a clean environment; care was taken to prevent external contamination. The test was performed with lab-grade reactants; therefore, the test did not have to consider the factors that are present in the refinery such as: higher temperatures, trace element compositions and fluid motion. The standard lab test did not include NOx sparging. Sparging with NOx will only be included in the refinery acid chloride reduction results. Although the level of chloride extraction when sparging the solution with dry air should have been higher

as the nitric acid strength increased, there was a possibility of contamination and human error that could have skewed the results.

4.1.3 Chloride Extraction from Refinery Samples

Refinery nitric acid samples were collected from May 6, 2010 to July 3, 2010. The initial tests in the lab included three blends of absorber to denitration scrubber acid: 3:1, 1:1 and 1:3. Table 8 and Figure 17 summarize the nitric acid strengths obtained from blending absorber and denitration scrubber acids.

Nitric Acid	Average Nitric Acid Strength
Absorber B	36.0%
Denitration Scrubber	50.0%
3:1 Volumetric Blend of Absorber to Denitration	40.0%
Scrubber	
2:1 Volumeric Blend of Absorber to Denitration	41.0%
Scrubber	
1:1 Volumetric Blend of Absorber to Denitration	43.0%
Scrubber	
1:2 Volumetric Blend of Absorber to Denitration	45.0%
Scrubber	
1:3 Volumetric Blend of Absorber to Denitration	46.0%
Scrubber	
1:1 Volumetric Blend of Absorber to Denitration	43.0%
Scrubber + NOx Purge	

Table 8: Acid Strengths of Blended Nitric Acids: Samples were collected from May 6, 2010 to July 3, 2010. The nitric acid strengths are an average strength calculated over the sample period. The total volume of blended acid for each test was 20.0mL.



Figure 17: Blended Nitric Acid Ratio Vs. Nitric Acid Strength: This figure is a visual representation of table 8. It is important to note that only the ratio of absorber B acid is plotted. The ratio of denitration scrubber acid can be calculated by 100-X, where X is the percentage of absorber B acid. The nitric acid strengths were calculated based on data obtained from May 6, 200 to July 3, 2010. The Y bar error represents the potential range of values based on two standard deviations.

Blending denitration scrubber acid with absorber acid provided a level of chloride extraction that increased with nitric acid strength. If absorber B acid was maintained at 37.0% and then blended with dentration scrubber acid at a 1:1 volumetric ratio, the resulting nitric acid blend would have strength of 44.0%. The average nitric acid strength for the 2:1 denitration scrubber to absorber acid blend was 45.0% during the sample period. Based on the nitric acid mass balance (see Section 4.4.1), 44.0 – 45.0% nitric acid can be obtained from blending absorber and denitration scrubber acid.

A 1:1 volumetric blend was used for the NOx purge. The level of chloride extraction using NOx sparging, as well as a combination of NOx and dry air sparging, was significantly higher than sparging with only dry air or NOx individually. As discussed in Section 4.1.2, oxygen provided a significant amount of chloride oxidation from sparging each solution with dry air.

NOx gas was only sparged for 30.0 seconds at 15.0psi (around 2.0kg/hr) in order to reflect the actual NOx flow rate that would be applied to the chloride reactors in the refinery. At this flow rate, insufficient

amounts of nitric acid would have been formed to increase the nitric acid strength above 43.0% [44]. Table 9 and Figure 18 present the level of chloride extraction for each alternative discussed in Section 3.3.

Volumetric Blend Ratio of Absorber B Acid to Denitration Scrubber Acid	Chloride Extraction Without Dry Air or NOx Purge	Chloride Extraction With Dry Air Purge	Chloride Extraction With NOx Purge	Chloride Extraction With NOx + Air Purge
3:1	7.0%	20.2%	N/A	N/A
2:1	10.0%	25.3%	N/A	N/A
1:1	13.7%	28.4%	66.4%	76.7%
1:2	14.7%	36.7%	N/A	N/A
1:3	16.8%	41.8%	N/A	N/A

Table 9: Chloride Extraction Level for Various Nitric Acid Blends and Alternatives: Samples were collected and prepared in the lab from May 6, 2010 to July 3, 2010. The chloride removal yields are average yields calculated over the sample period. The total volume of each blended acid prepared and tested was 20mL.



Figure 18: Nitric Acid Blend Vs. Level of Chloride Extraction: Samples were collected and prepared in the lab from May 6, 2010 to July 3, 2010. The level of chloride extraction was calculated over the sample period. The total volume of each blended acid prepared and tested was 20.0mL. The Y bar error represents the potential range of values based on two standard deviations. As shown in this Figure, there were fewer sample points for Blend + NOx and Blend + Air + NOx samples.

An important consideration that will have to be factored into the level of chloride extraction is the residence time of nitric acid in the eductor pumps of the chloride reactors. Blended acid samples were sparged with dry air for 1 minute at 4psi. A separate 1:1 nitric acid blend was sparged with NOx for 30.0 seconds at 15.0psi. Nitric acid in the eductor pumps of the chloride reactors resides for up to 10.0 hours [34]. Therefore, the results obtained from the sampling and lab tests will likely increase dramatically in the circuit due to this increased residence time of nitric acid in the eductor pumps of the chloride reactors. The nitric acid will be contacted many times over by the sparged air and/or NOx, which will ultimately increase the rate (kg/hr) of chloride extracted.

The average chloride concentration in the 1:1 blended acid during the test period was 800.0mg/L Cl. The average temperature of the blended acids was 27.0°C. There was an average chloride extraction of 28.4% associated with blending the nitric acid to 43.0% and sparging the solution with dry air. Unlike the standard lab test, there were very little nitric acid fumes produced from the refinery nitric acid due to the color of the NOx fumes being emitted off the acid. The color was a dark brownish-red, which is

characteristic of nitric oxide, nitrous oxide, nitrogen dioxide and dinitrogen tetraoxide fumes as the primary components of the NOx gas. By far the biggest component of the NOx fumes was nitrogen dioxide (>99.0%). Recall from reaction 3 that nitric oxide is formed when nitrogen dioxide reacts with water:

$$3NO_2(g) + H_2O(l) \rightarrow 2HNO_3(l) + NO(g)$$
 (3)

The presence of dissolved nitrogen dioxide in the refinery nitric acid results from the flow of NOx gas into the absorber tanks [42]. Nitrogen dioxide reacts with the water present in the nitric acid to produce nitric oxide. Chloride ions were able to be further oxidized by nitric oxide due to the increased nitric acid strength that provided a greater concentration of hydrogen ions. The increased concentration of hydrogen ions drove the oxidation reaction more aggressively:

$$2NO(g) + 2H^{+}(aq) + 2Cl^{-}(aq) \rightarrow N_{2}0(g) + H_{2}0(l) + Cl_{2}(g)$$
(16)

As previously discussed, sparging the blended acids with dry air provided additional oxidation of chloride ions due to the presence of oxygen (~16.0% composition) in the air [35].

The anticipated flow rate of 1:1 blended nitric acid (i.e., equal flow rates of absorber B and denitration scrubber acid) through the chloride reactors will be 2.0m³/hr (discussed in Section 4.4). Based on the average level of chloride extraction of 28.4% for 1:1 blended acid sparged with dry air, the following chloride extraction rate would theoretically be obtained by sparging 43.0% nitric acid with 4psi of dry air (based on the average 800.0mg/L concentration of chloride during the test period):

$$(0.80 \text{kg/m}^3) \ge (0.284) = 0.23 \text{kg/m}^3$$

$$(0.23 \text{kg/m}^3) \times (2.0 \text{m}^3/\text{hr}) = 0.46 \text{kg/hr}$$

Removing 0.46kg/hr of chloride from the nitric acid is low compared to the potential level of chloride extraction that could occur in the refinery. The conditions in the nitric acid circuit would yield a greater level of chloride extraction due to elevated temperatures and flow pressures. Recall from Figure 15 that chloride concentrations at 37.0% nitric acid compared to 43.0% were 90.0% lower in the nitric acid recovery circuit. Although most of the chloride was converted to chlorine and remained inside the recovery circuit, this presented a unique opportunity. If 37.0% nitric acid from the absorber is properly bled with 50.0% denitration scrubber acid right in front of the chloride reactors, then the level of chloride extraction can potentially reach as high as 90.0% from blending the acids alone.

The average chloride concentration for the 1:1 acid blend used for NOx sparging was 460.0mg/L during the test period. Sparging the blended acids with NOx drastically increased the level of chloride extraction during the lab tests. The dramatic increase was the result of four important factors: concentration of nitric oxide, concentration of hydrogen ions, flow pressure and temperature. Sparging the solution with NOx instead of dry air dramatically increased the concentration of nitric oxide in the nitric acid due to the reaction between nitrogen dioxide and water. The greater concentration of nitric oxide contributed largely to the level of chloride extraction, since more chloride ions were contacted and oxidized in the solution. Also, the temperature and flow pressure of the NOx gas being sparged through the 1:1 blended acid was consistently around 200.0°C and 15.0psi. As a result, the level of chloride extraction was much higher.

The maximum rate to purge NOx through the blended nitric acid would be 2.0 kg/hr based on the environmental implications (discussed in section 4.3). The amount of chloride oxidized to chlorine depends on the ratio of nitric oxide to chloride. Recall from reaction 3 that one mole of nitric oxide was produced for every three moles of nitrogen dioxide reacting with one mole of water. The NOx gas being sparged from the Spencer turbines was almost entirely nitrogen dioxide. One mole of nitric oxide was required to oxidize one mole of chloride in terms of stoichiometry (reaction 18). Therefore, if the average uptake of nitrogen dioxide into the nitric acid is 55.0% [42] then a flow rate of 2.0kg/hr of NOx gas would have theorectially produced:

2.0kg/hr (0.55) = 1.1kg/hr of NO₂ absorbed into the nitric acid

 $(1.1 \text{kg/hr NO}_2) / (0.046 \text{kg/mol}) = 24.0 \text{mol/hr of NO}_2 \text{ absorbed}$

Since the ratio was one mole of nitric oxide produced per three moles of nitrogen dioxide absorbed, then 8.0mol/hr of nitric oxide would have been produced when 2.0kg/hr of NOx (as NO₂) was sparged into the nitric acid. In terms of chloride extraction, sparging 2.0kg/hr of NOx would have produced the following theoretical chloride extraction rate:

 $(8.0 \text{mol/hr}) \ge (0.030 \text{kg/mol}) = 0.24 \text{kg/hr}$

Therefore, ~0.24kg/hr of chloride would theoretically be extracted when 2.0kg/hr of NOx was sparged through the nitric acid. This amounted to a theoretical level of chloride extraction of 26.1%. The additional air sparging would have produced additional oxidation, since oxygen would have contributed additional oxidation of chloride ions.

A combination of dry air and NOx sparging would have theorectially extracted ~0.70kg/hr (i.e., 0.46kg/hr + 0.24kg/hr). A 0.70kg/hr chloride extraction rate amounts to a theorectical level of chloride extraction of 69.6%. However, the level of chloride extraction for both alternatives 3 (air sparge) and 4 (air and NOx sparge) were higher than the predicted stoichiometry. Similar results were observed by Pierce et al. (2007) during their research. They discovered that the level of chloride extraction was higher than the stoichiometry of the reactions when acid concentrations were above 8M (40.0%), which is similar to what occurred during the refinery sample tests [33].

Recall reaction 3 in section 2.2.4 [35]:

$$3NO_2(g) + H_2O(l) \rightarrow 2HNO_3(l) + NO(g)$$
 (3)

And recall from reaction 16 that nitric oxide will oxidize all of the chloride ions it comes into contact with in solution:

$$2NO(g) + 2H^{+}(aq) + 2CI^{-}(aq) \rightarrow N_{2}O(g) + H_{2}O(l) + CI_{2}(g)$$
(16)

The reason for additional chloride removal observed was due to the formation of nitrous oxide as a secondary product to the oxidation of chloride by nitric oxide. Nitrous oxide is an ever stronger oxidant than nitric oxide, since it has an ORP value of 1.766 V in 1.0 M nitric acid [35]. In order for nitrous oxide to oxidize chloride ions there must be a high concentration of hydrogen ions left over from reaction 18 in order to occur. Based on the level of chloride extractioin (i.e., higher level of chloride extraction than predicted stoichiometrically), 43.0% nitric acid strength provided enough hydrogen ions to drive the secondary reaction between nitrous oxide and chloride ions:

$$N_2O(g) + 2H^+(aq) + 2CI^-(aq) \rightarrow N_2(g) + H_2O(l) + Cl_2(g)$$
 (17)

This secondary reaction explains the additional chloride oxidation that Pierce et al. (2007) did not discover during their research and the reason why additional chloride was removed during the lab simulations. The formation of nitrous oxide occurred at a rate of 2.0 moles of nitric oxide per mole of nitrous oxide. Therefore, if 8.0 moles/hr of nitric oxide were formed when 2.0kg/hr of NOx was sparged through the acid, then there would have been 4.0 moles/hr of nitrous oxide formed. The molar ratio for removing chloride with nitrous oxide is two times greater than what was expected with only nitric oxide. The additional rate of chloride removal would therefore be:

 $(4.0 \text{ moles/hr}) \ge (0.030 \text{kg/mol}) = 0.12 \text{kg/hr}$
Since there were two moles of chloride ions oxidized per mole of nitrous oxide, 0.24kg/hr of additional chloride ions were oxidized. Therefore, based on the stoichiometry of the associated reactions, sparging the nitric acid with NOx gas only should have had a chloride extraction rate of 0.36kg/hr and sparging the 43.0% blended nitric acid with both dry and NOx gas should have had a chloride extraction rate of 0.88kg/hr.

In terms of chloride extraction levels, sparging 43.0% blended nitric acids with NOx gas should have had an average extraction yield of 41.7% and sparging 43.0% blended nitric acid with both dry and NOx gas should have had a chloride extraction yield of 95.0%. Comparing these results to the actual reduction yields of 66.4% and 76.7% (see Appendix A) revealed that human error and nitric acid contamination (trace metals) likely occurred during the lab tests. Therefore, the overall confidence level for laboratory sparging tests was:

 $[(41.7 / 66.4) + (76.7 / 95.0)] \times 100\% = 72.0\%$ confidence level

An important factor that must also be considered was the effect that trace metal compositions had on the relative oxidation of chloride during lab tests. Pierce et al. (2007) conducted their research using pure nitric acid [33]. As a result, their research could not be used to demonstrate the impact of trace metal contamination, which would most likely be present in most industrial facilities. Therefore, understanding the effect of trace metal contamination will provide necessary information to understand the observed the level of chloride extraction from contaminated nitric acid.

Trace metals, as discussed in section 2.3.4, could have been easily oxidized by nitric oxide and nitrous oxide. Therefore, the presence of trace metals could have reduced the level of chloride extraction. Lakefield Research Inc. (2010) is contracted by the BRR to conduct periodical tests on trace compositions in the various nitric acids in the circuit. According to the monthly progress report for April 2010 [66] the following trace metals were considered to have significant concentrations in the absorber acid: calcium (42.2mg/mg/L), magnesium (4.32mg/L), sodium (40.2mg/L), and silicon (9.1mg/L) (Lakefield Research Inc, 2010). The ORP values for all of these trace metals are well below the ORP value for chlorine. In fact, magnesium is the least noble metal in the galvanic series and is very easily oxidized. Oxygen, nitic oxide and nitrous oxide are strong enough to oxidize all of these trace metals in the nitric acid [35]. Therefore, all of these trace metals would be oxidized before any chloride ions were oxidized by oxygen, nitric oxide and nitrous oxide, which produces a negative impact for chloride extraction.

The concentrations of trace metals in the denitration scrubber acid were equally as important as the concentrations in the absorber acid, since both acids would be blended. Denitration scrubber nitric acid had the following trace metal concentrations in April, 2010: iron (7.6mg/L), sodium (8.67mg/L), silicon (22.9mg/L) and uranium (15.6mg/L) [66]. Once again each trace metal has a significantly lower ORP than chlorine and would have been oxidized before any chloride ions in solution.

4.2 Cost Comparisons

Administrative data from 2009 was analyzed in order to determine the costs associated with the current chloride removal circuit. This data was also used to predict the costs of applying the alternative chloride removal circuits at the BRR.

4.2.1 Chloride Removal Circuit Energy Costs:

Power from the pumping system:

The total power draw for the pumping system was 107.58 hp [19]. It is important to note that the 0.9 factor takes into account the efficiency of the electric motor for the pumping system (i.e., electrical motors are usuall 90% efficient or better) [19]. Therefore, converting horsepower to kilowatt-hours, the average power draw in 2009 was:

 $(107.58hp / 0.9) \ge (0.746 \text{ kW} / hp) = 89.18 \text{ kW}$

The energy cost for the BRR from the power grid was \$0.07/kWh in 2009 [19]. Therefore, the annual cost of the pumping system for 2009 was:

 $(89.18 \text{kW}) \ge (24 \text{ hours}) \ge (\$0.07/\text{kWh}) = \$149.82 \text{ per operating day}$

(\$149.82 / operating day) x (240 operating days / year) = \$35 956.80 / year

Ozone Generator Power Draw:

The total power draw for the ozone generator (dielectrics) was 121.4 kW [19]. Therefore, the annual energy cost to operate the ozone generator in 2009 was:

 $(121.4kW) \times (24 \text{ hours / day}) \times (\$0.07kWh) = \$203.95 \text{ per operating day}$

(\$203.95 / operating day) x (240 operating days / year) = \$48 948.00 per year

Total Chloride Removal Circuit Energy Costs:

The annual cost to power the chloride removal circuit in 2009 was:

\$35 956.8 + \$48 948.0 = \$84 904.80 per year

4.2.2 Air Circuit Costs

The power draw for the air compressor and air dyer in the powerhouse associated with air flow to the chloride reactors was conservatively estimated to be 3 horsepower from Cameco's chief powerhouse engineer Mike Stortini (2009) [60]:

 $(3.0hp / 0.9) \ge (0.746 \text{ kW} / hp) = 2.5 \text{ kW}$

The air circuit is run roughly 80% (20 hours) of the operating day. Therefore, the annual energy cost to operate the air circuit in 2009 was:

(2.5 kW) x (20 hours/operating day) x (240 operating days/year) x (\$0.07/kWh) = \$840.00 per year

For the purpose of this research, the total annual energy cost for the NOx fuming line pump will be assumed to be \$0.00 since the Spencer turbine has sufficient pressure to pump the required NOx to the chloride reactors. The cost to pump the nitric acid from the denitration scrubber tank to the absorber nitric acid line in front of the first chloride reactor was also estimated to be \$0.00 since the acid is already being pumped to the top floor of digestion, which is the same elevation as the top of the chloride reactors.

4.2.3 Summary of Total Costs

It is important to note that the pump system annual cost of \$35 956.80 per year for the chloride removal circuit will remain for alternatives 2-6. However, all six alternatives would require a 304-stainless steel pipe running from the bottom of the denitration scrubber tanks to the chloride reactor areas. The denitration scrubber pipe would bleed denitration scrubber acid into the absorber nitric acid at a volumetric ratio based on the results of the research and the mass/balance of the denitration scrubber acid. The nitric acid line running from the denitration scrubber tank would have to be built with seamless 304-stainless steel at schedule 40. The schedule indicates the thickness of the stainless steel. The conservative estimated distance from the denitration scrubber tank to the chloride reactors is 180 feet. A 1" or $1 \frac{1}{2}$ " line would most likely be required to accommodate for this flow rate. Therefore, the installation cost would be around \$5000.00 [46].

Alternatives 3 and 4 would require a NOx gas fuming line from the Spencer turbine to the chloride reactors. The conservative estimated distance from the Spencer turbine to the chloride reactors is around 200 feet [46]. The NOx gas fuming line would be constructed with different 304-stainless steel specifications. The NOx fuming line running from the Spencer turbine to the chloride reactors would have to be built with seamless 304-stainless steel at schedule 10. Again, a 1" or 1 ½" line would most likely be required to accommodate for this flow rate of NOx gas. Therefore, the installation cost would also be around \$5000.00 [46]. Table 10 summarizes the total costs for the current chloride removal circuits and all six of the proposed alternative circuits; however, installation costs will be neglected in the annual calculation since they are a one-time cost [46]:

	Operational Cost (per year)	Installation Costs	Total Cost (per year)
Current Chloride	Ozone Generator: \$48 948.00	None	\$84 904.80
Removal Circuit			
(Ozone Purge)	Acid Pump System: \$35 956.80		
Alternative #1:	Bleeding Line Pump: \$0 Bleeding Line: \$5000.00		\$0.00
Blend Without			
Purge	Acid Pump System: \$0		
Alternative #2:	Bleeding Line Pump: \$0.00	Bleeding Line: \$5000.00	\$35 956.80
Blended + Air			
Purge	Air Circuit Pump: \$840.00		
	Acid Pump System: \$35 956.80		
Alternative #3:	Bleeding Line Pump: \$0.00	Bleeding Line: \$5000.00	\$ <mark>36 796.8</mark> 0
Blend + NOx Purge			

	Air Circuit Pump: \$840.00	NOx Line: \$5000.00	
	Acid Pump System: \$35 956.80		
Alternative #4:	Bleeding Line Pump: \$0.00	Bleeding Line: \$5000	\$36 796.80
Blend + Air Purge			
+ NOx purge	NOx Line Pump: \$0.00	NOx Line: \$5000.00	
	Air Circuit Pump: \$840.00		
	Acid Pump System: \$35 956.80		
Alternative #5:	Bleeding Line Pump: \$0.00	Bleeding Line: \$5000.00	\$39 296.80
Blend + Air Purge	Ozone Purge: \$2500.00		
+ Periodical Ozone			
Flush	Air Circuit Pump: \$840.00		
	-		
	Acid Pump System: \$35 956.80		
Alternative #6:	Bleeding Line Pump: \$0.00	Bleeding Line: \$5000.00	\$84 904.80
Blend + Ozone			
Purge	Ozone Generator: \$48 948.00		
	Acid Pump System: \$35 956.80		

 Table 10: Summary of Costs Analysis: The annual cost for the current chloride removal circuit and each alternative included operational costs only. It does not include installation, repair and maintenance costs.

4.3 Environmental Impacts Comparisons

4.3.1 Direct Emissions and Associated Impacts

One concern regarding the alternative chloride removal system is uranium concentrations in the plant effluent discharge. The concentration of uranium in the denitration scrubber acid in 2009 was 7.5g/L [47]. Under the current operating conditions, the denitration acid does not flow through the chloride removal circuit. It is pumped directly to the solvent extraction circuit and the digestion circuit through the nitric acid rundown tanks. The average concentration of uranium in the plant effluent discharge in 2009 was 0.024mg/L [48]. Therefore, under the current operating conditions, the concentration of uranium in the denitration scrubber acid is not important for plant effluent discharge because it does not flow through the system. The alternative chloride removal circuit would bleed the denitration scrubber acid in with the absorber acid. Therefore, the nitric acid flowing through the chloride reactors would have greater amounts

or uranium compared to the current chloride removal circuit. However, the risk of having uranium in the plant effluent is virtually negligible. This is due to the fact that uranium would not be evaporated as an off-gas exiting the chloride reactors. It would remain in the nitric acid and would flow back through the circuit [42].

Although there is no upper limit on the release of uranium in plant effluent in Ontario Regulation 560/94: Effluent Monitoring and Effluent Limits – Metal Mining Sector [49], the Canadian Nuclear Safety Commission (CNSC) had set maximum discharge levels for the BRR. The Nuclear Fuel Facility Operating License (2007) is provided by the CNSC regarding maximum discharge levels for the BRR [50]. The BRR operating license has established a maximum allowable discharge concentration of uranium of 20.0mg/L U in the plant effluent [50]. Therefore, the 0.024mg/L U average concentration for 2009 fell well below the maximum discharge levels issued by the CNSC. Therefore, the risk of having dangerous uranium concentrations in the plant effluent is negligible.

Increasing uranium concentrations in the nitric acid passing through the chloride reactors also poses the threat of having uranium particulate emitted out the absorber stack. In 2009, the average uranium grab sample from the absorber stack was 0.01mg/m³ of uranium [51]. The BRR operating license (2007) has a maximum discharge level of 2.0 kg/hr of uranium into the atmosphere [50]. Therefore, the uranium particulate emission fell well below the upper limit set by the CNSC in 2009. The melting point of uranium is 1132.0°C [35]. Operating temperatures and pressures through the chloride removal circuit came nowhere near this temperature [34]. Losing additional uranium out the absorber stack is therefore not a concern.

An important environmental concern involved with an alternative chloride removal circuit, most notably alternatives 3 and 4, is an increase in NOx emission out the absorber stack. Recall that the off-gases (primarily ozone and NOx) from the caustic scrubber in the chloride removal circuit flow, via negative pressure, to the ozone destructor [34]. Although the ozone destructor manages to eliminate most of the ozone, it does not destroy the additional NOx gas that escapes from the scrubber solution. The atmospheric release of ozone out the absorber stack is not sampled regularly. However, there is an online NOx analyzer that continuously monitors the atmospheric release of NOx gas out the absorber stack [42].

The release of NOx is logged as a flow rate in the AS 400 system. The average flow rate of NOx released out the absorber stack in 2009 was 4.8 kg/hr [52]. Over the entire 240 operational day there was a total of 27,648kg of NOx released into the atmosphere in 2009. NOx emissions at the BRR are regulated by the Canadian Nuclear Safety Commission (CNSC). The CNSC has set maximum emission levels for the

BRR in the operating license (2007). The CNSC's nuclear fuel facility operating license for the BRR has established a maximum flow rate of NOx out the absorber stack at 15.0 kg/hr [50].

The potential for increased NOx emissions would be most prevalent for alternatives 3 and 4. As nitric acid becomes stronger, NOx solubility in the acid decreases [35]. If NOx gas were sparged through the nitric acid in the chloride reactors, additional NOx would flow out the absorber stack. Recall that ~55.0% of the NOx gas (as NO₂) is absorbed into the nitric acid, which means that 45.0% of the remaining NOx gas would flow to the caustic scrubber and absorber stack off the top of the three chloride reactors [42]. If 2.0kg/hr of NOx were sparged through the chloride eductor pumps, then the following concentrations of NOx would be added:

$(2.0 \text{kg/hr}) \ge (0.45) = 0.9 \text{kg/hr}$

Roughly 1/3 of the NOx gas is absorbed in the caustic scrubber fluid [42]. Therefore, 0.6kg/hr of additional NOx gas would be emitted out of the absorber stack. Recall that the average flow rate of NOx out the absorber stack in 2009 was 4.8kg/hr. Therefore, the NOx emission rate would increase up to 5.4kg/hr if 2.0kg/hr of NOx were sparged through the chloride reactors, which is well below the 15.0kg/hr upper limit in the BRR operating license [50]. Modifications to the NOx chiller system can potentially mitigate this slight increase of NOx emissions generated by fuming 2.0kg/hr of NOx through the chloride reactors. In fact, modifications to the NOx chilling system are planned for the near future and expect to reduce NOx emission below 2.0 kg/hr out of the absorber stack.

The nitric acid strength of the blended acids will be 7.0% stronger than the nitric acid strength currently flowing through the chloride reactors. Therefore, additional NOx will be emitted from the stronger nitric acid as it flows through the chloride reactors. The amount of NOx that would be emitted from the blended acid is difficult to predict and would require close monitoring to ensure that levels are not too elevated. Also, a combination of NOx and air sparging for alternative 4 will produce additional NOx emissions than predicted above. Emission levels can be controlled by reducing either the NOx fume line flow rate and/or the plant air flow rate to the bottom of the chloride reactors. Also, as discussed above, modifications to the NOx chilling system will reduce the level of NOx emission out of the absorber stack.

Another important environmental impact that could be generated by an alternative chloride removal circuit, especially alternatives 3 and 4, is a slight increase of nitrate and nitrite levels in the plant effluent discharge. Nitrate and nitrite concentrations are only sampled at two sampling points: the pipe entry into the blowdown tank in the chloride removal circuit and from the plant effluent. The average concentration

of nitrate in the plant effluent discharge in 2009 was 30.20mg/L [53]. The average concentration of nitrite in the plant effluent discharge was 2.91mg/L in 2009 [53]. Recall that air is pumped into the aeration tank and hydrogen peroxide is added to convert the nitrites into nitrates prior to being sent to the treatment lagoons. In terms of conversion efficiency, an average of 80% of nitrite is converted to nitrate in the aeration tank [42].

Recall that 1/3 of the NOx gas emitted as off-gas from the chloride reactors is absorbed into the caustic scrubber fluid [42]. If 0.9kg/hr of NOx were emitted through the chloride reactor off-gas line, an additional 0.3kg/hr of NOx (as NO₂) would be absorbed in the caustic scrubber fluid as nitrite. The additional nitrite would then flow down through the blowdown aeration tank and end up in the plant effluent discharge as nitrate or nitrite. The plant effluent was discharged at an average rate of 30.0m³/hr [42]. Therefore, if 2.0kg/hr NOx were sparged through the nitric acid in the chloride reactors the additional concentration of nitrate and nitrite emitted in the plant effluent would be:

 $[(0.3 \text{kg/hr}) \times (0.80)] / (30.0 \text{m}^3/\text{hr}) = 0.008 \text{kg/m}^3 = 8.0 \text{mg/L} \text{ of nitrate}$

 $[(0.3 \text{kg/hr}) \times (0.20)] / (30.0 \text{m}^3/\text{hr}) = 0.002 \text{kg/m}^3 = 2.0 \text{mg/L of nitrite}$

The total emission concentrations of nitrate/nitrite in the plant effluent could increase from 30.20mg/L and 2.91mg/L up to 38.20mg/L and 4.91mg/L respectively. This increase in nitrate/nitrite concentrations would still be well below the upper limits of 100.0mg/L and 10.0mg/L set by the CNSC [50]. However, it is still an important environmental impact that must be considered. Additional nitrate and nitrite releases could be mitigated by reducing the nitric acid strength in the concentrators and improving to the NOx chiller system. However, an environmental impact debate arises whether the reduction in energy and material use outweighs the slight increase in NOx and nitrate/nitrite emissions.

The BRR is subject to the Metal Mining Sector within the Canadian Environmental Protection Act (CEPA) [54]. The BRR is regulated according to Ontario Regulation 560/94 'Effluent Monitoring and Effluent Limits' [49]. The Municipal and Industrial Strategy for Abatement (MISA) monitors the plant effluent discharges at the BRR in order to ensure compliance with MOE regulations. Even though there are no upper limit levels for nitrite concentrations in water effluent discharge, the BRR is subject to section 26 of Ontario Regulation 560/94 (toxicity test using the lethality of rainbow trout) [49]. According to the regulation, a minimum of 50.0% of rainbow trout must survive the water quality test [49]. The acute lethality test using rainbow trout is a biological test method mandated by Environment

Canada (EC) for testing effluent water quality; however, the legislation on LC50 levels for rainbow varies from province to province [55].

MISA performs a toxicity test of the BRR effluent water once per quarter for every calendar year. Nitrite in the water effluent became dangerous for rainbow trout when concentrations surpassed 12.0mg/L (i.e., the LC50) [57]. However, the confidence rate of the rainbow trout tests is very low since there are several other chemicals, such as cyanide, that drastically affect the LC50 of rainbow trout and prevent an accurate nitrite concentration threshold [53]. Therefore, the LC50 test failure cannot solely be attributed to either cyanide or nitrite, but a combination of both [53]. The average nitrite concentration in the BRR effluent discharge for 2009 was 2.91mg/L, which is well below the LC50 of rainbow trout [53]. In order to evaluate the cumulative impact of nitrate and nitrite levels, data from 2000 to 2005 was evaluated regarding their concentrations during MISA rainbow trout toxicity tests. Rainbow trout are highly sensitive to nitrate and nitrite concentrations in the local environment and serve as a good indicator of the potential environmental impacts of slightly increasing nitrite concentrations in local water systems [56].

MISA toxicity tests from 2000 to 2005 [57] were compared to concentrations of nitrate and nitrite near and above 38.20mg/L nitrate and 4.91mg/L nitrite (i.e., predicted concentrations from NOx sparging). As previously mentioned, the concentration of cyanide is another environmental toxicant that is lethal for rainbow trout [53] and was therefore considered for evaluating the impact of nitrate and nitrite concentrations. MISA toxicity tests for nitrate and nitrite concentrations around 38.20mg/L and 4.91mg/L were only evaluated when cyanide concentrations were low (below 80.0ug/L) in an attempt to negate the effect of cyanide.

In October 2004, there were two MISA toxicity tests performed. The concentrations of nitrate were 53.40mg/L and 82.70mg/L. The concentrations of nitrite were 8.05mg/L and 8.40mg/L. Cyanide concentrations were 14.00ug/L for both tests. There were no rainbow trout that were killed at these concentrations. Similarly, MISA tests performed in April 2004 had no rainbow trout deaths when concentrations of nitrates were 50.9mg/L and 68.6mg/L; nitrites were 5.42mg/L and 5.68mg/L; and cyanides were 49.00ug/L and 78.00ug/L. The same results appeared over and over for these concentrations ranges during the period of 2000 to 2005 [57] (see Appendix A for 2000-2005 data). Although nitrate, nitrite and cyanide concentrations were periodically above the upper limits mandated by the CNSC operating license for the BRR (2007), cumulative environmental impacts were not observed over the five year period. Therefore, the slight increase in nitrate and nitrite concentrations from alternative 4 will remain well below the upper limits mandated in the CNSC operating license (2007) and

would not produce adverse environmental impacts. However, proper monitoring will be required to ensure that cumulative effects do not occur over for time periods greater than five years.

It is important to note that one element of concern was that elevated concentrations of nitrites in the plant effluent could have been caused in similar ways by the off-gas scrubber system. The first cause may have occured during the initial filling of the chloride reactor followed by aeration. A significant amount of NOx would have been sparged when strong acid was first aerated. Scrubbing an abnormally high volume of NOx gas would have resulted in high nitrate and nitrite concentrations in the caustic soda scrubber blowdown tank. The second cause of elevated nitrites could have been a failure or malfunction of the peroxide pumps. The third cause of elevated nitrites could have been potentially caused by a localized air loss to the aeration tank due to component failure. The fourth likely cause of elevated nitrite concentrations in the effluent could have been due to improper dosing rates of peroxide into the scrubber blowdown [42]. If these scenarios occurred frequently in the off-gas scrubber system then they would have contributed largely to the concentrations in the plant effluent discharge may not rise if the off-gas scrubber system is carefully operated and monitored. Modifications to the NOx chiller system could also potentially reduce NOx, nitrate and nitrite emission below the averages in 2009.

4.3.2 Energy Consumption and Relative CO₂ Emissions

An important environmental impact consideration involved the relative amount of carbon dioxide emissions produced for the energy requirement to the current chloride removal circuit. The calculations considered for the current circuit and proposed alternatives were based on the process described by Masters and Ela (2008) [58]. Recall that the power draw for the chloride removal circuit was an average of 210.6 kW in 2009 [19]. Therefore, over the course of 240 operating days, the total amount of energy required to power the circuit was (210.6 kW) x (24 hrs / operating day) x (240 operating days / year) = $1.20 \times 10^6 \text{ kW}$ / year. This is an energy requirement, not a power requirement; therefore, the units are in kilowatt-hours. Converting kilowatt-hours to mega-joules [35]:

 $(1.20 \times 10^{6} \text{ kW} / \text{year}) \times (3.6 \text{MJ} / \text{kW}) = 4.32 \times 10^{6} \text{ MJ}$ per year

Only the combustion stage of energy production that feeds the Ontario Power Grid was considered. The average energy conversion efficiency was assumed to be 30.0% [58]:

 $(4.32 \times 10^6 \text{ MJ} / \text{year}) \times (1 \text{ MJ} / 0.3 \text{ MJ}) = 1.44 \times 10^7 \text{ MJ} / \text{year}$ of equivalent fuel energy from the Ontario Power Grid was required to meet the demand of the current chloride removal circuit [59].

There are several databases that contain information regarding energy sources and carbon intensities in Ontario. For the purposes of this thesis, data was obtained from the Independent Electricity System Operator (IESO) in order to calculate relative carbon dioxide emissions for 2009,The IESO provided the following energy sources in Ontario for 2009 [59]:

- nuclear (37%);
- hydro (26%);
- wind/solar/biomass (1%);
- coal (29%); and
- natural gas (7%).

The first three energy inputs (nuclear, hydro, and renewable) were assumed to generate zero carbon dioxide emissions in terms of the combustion stage of energy production, which will be the functional unit for this calculation [58]. For coal and natural gas, the following carbon intensities (in terms of grams of carbon emitted per mega-joule combusted) were assumed to be [58]:

- coal: 25.8 gC/MJ; and
- natural gas: 15.3 gC/MJ.

In terms of carbon intensity for the Ontario Power Grid, the relative intensities of coal and natural gas were:

 $[(0.29) \times (25.8 \text{ gC/MJ})] + [(0.07) \times (15.3 \text{ gC/MJ})] = 8.6 \text{ gC/MJ}$

This meant that for every mega-joule energy produced for the Ontario Power Grid had an equivalent of 8.6 grams of carbon emitted at the combustion stage. According to this relative carbon dioxide emission, the BRR chloride removal circuit emitted the following relative amount of carbon dioxide in 2009:

 $(1.44 \text{ x } 10^7 \text{ MJ} / \text{year}) \text{ x } (8.6 \text{ gC/MJ}) = 1.24 \text{ x } 10^8 \text{ gC} / \text{year} = 1.24 \text{ x } 10^5 \text{ kgC}$ per year

There are 44g of CO_2 for every 12g of carbon. Therefore, carbon dioxide emissions for the chloride removal circuit in 2009 were:

 $(1.24 \text{ x } 10^5 \text{ kgC} / \text{ year}) \text{ x } (44 \text{ g } \text{CO}_2 / 12 \text{ g } \text{C}) = 4.55 \text{ x } 10^5 \text{ kg } \text{CO}_2$

Alternative 1: Relative CO₂ Emissions

The relative carbon dioxide emissions associated with blending denitration scrubber acid and absorber acid would be similar to the relative emissions associated with the current pumping system. The energy draw for pumping nitric acid from the denitration scrubber tank to the absorber line in the chloride removal circuit is negligible for calculating relative carbon dioxide emissions. Therefore, the energy draw consideration for alternative 1 was the energy required for the pumping system:

Recall that the pumping system used an average of 89.2kW of power in 2009 [19]. Therefore, in terms of annual energy requirement, the total energy draw would be:

(89.2kW) x (24hrs / day) x (240 operating days / year) = 5.14×10^5 kW per year

Now, proceeding with the same steps as above:

 $(5.14 \text{ x } 10^5 \text{ kW} / \text{year}) \text{ x } (3.6 \text{MJ} / \text{kW}) = 1.85 \text{ x } 10^6 \text{ MJ}$ per year of energy required from provincial power grid. The carbon intensity for the provincial power grid is 8.6 gC/MJ. Therefore, the carbon intensity for alternative 1 would be:

 $(1.85 \times 10^{6} \text{ MJ} / \text{year}) \times (1.0 \text{ MJ} / 0.3 \text{ MJ}) = 6.7 \times 10^{6} \text{ MJ}$ per year

 $(8.6 \text{gC/MJ}) \times (6.7 \times 10^6 \text{ MJ} / \text{year}) = 5.30 \times 10^7 \text{ gC} / \text{year} = 5.30 \times 10^4 \text{ kgC}$ per year

The relative carbon dioxide emissions for alternative 1 would be:

 $(5.30 \text{ x } 10^4 \text{ kgC} / \text{ year}) \text{ x } (44 \text{gCO}_2 / 12 \text{g C}) = 1.94 \text{ x } 10^5 \text{ kg of CO}_2 \text{ per year}$

Alternative 2: Relative CO₂ Emissions

Alternative 2 would have to consider the relative carbon dioxide emissions associated with the current pump system, as well as the powerhouse air pump system. As calculated for alternative 1, the relative carbon dioxide emissions for the current pumping circuit would be 1.94×10^5 kg of CO₂ based on 2009

figures. The total power draw for the air system in the powerhouse is 3.0 hp [60]. This is a conservative value that accounts for the air pumps, compressor and drier. Converting horsepower to kilowatt-hours:

 $(3hp / 0.9) \ge (0.746kW / hp) = 2.5kW (24 hours / day) = 60kW per operating day$

The total annual power would be:

 $(60 \text{kW} / \text{operating day}) \text{ x} (240 \text{ operating days} / \text{year}) = 1.44 \text{ x} 10^4 \text{ kW per year}.$

Converting kilowatts to mega-joules:

 $(1.44 \text{ x } 10^4 \text{ kW / year}) \text{ x } (3.6 \text{MJ} / \text{kW}) = 5.18 \text{ x } 10^4 \text{ MJ}$ per year

 $(5.18 \times 10^4 \text{ MJ} / \text{year}) \propto (1\text{MJ} / 0.3\text{MJ}) = 1.73 \times 10^5 \text{ MJ}$ per year of energy would be required from provincial power grid generation according to 2009 figures. As previously mentioned, the carbon intensity for the provincial power grid is 8.6 gC/MJ. The carbon intensity for alternative 2 would be:

 $(8.6 \text{gC/MJ}) \ge (1.73 \ge 10^5 \text{ MJ} / \text{year}) = 1.49 \ge 10^6 \text{ gC} / \text{year} = 1.49 \ge 10^3 \text{ kgC} / \text{year}$

 $(1.49 \times 10^3 \text{ kgC} / \text{ year}) \propto (44\text{gCO}_2 / 12\text{g C}) = 5.45 \times 10^3 \text{ kg}$ of CO₂ emitted per year to power the powerhouse dry air system.

Therefore, the relative carbon dioxide emissions for alternative 2 would be:

 $(1.94 \text{ x } 10^5 \text{ kg CO}_2 / \text{ year}) + (5.45 \text{ x } 10^3 \text{ kg of CO}_2 / \text{ year}) = 2.0 \text{ x } 10^5 \text{ kg CO}_2 / \text{ year}$

Alternative 3: Relative CO₂ Emissions

The relative carbon dioxide emissions associated with alternative 3 would have to consider the power draw for the nitric acid pump from the denitration scrubber tank to the absorber acid line in the chloride removal circuit. It would also have to consider the power draw for pumping NOx from the Spencer turbines to the chloride reactors. These two energy considerations for relative carbon dioxide emissions were supplemental to the emissions associated to the pumping system, which had a value of $1.94 \times 10^5 \text{ kg}$ of CO₂ / year. A conservative estimate for the total power requirement for the NOx and nitric acid pumping system would be 2.0hp [60]. Converting horsepower to kilowatt-hours:

 $(2.0hp / 0.9) \ge (0.746 kW / hp) = 1.66 kW.$

Following similar steps as alternative 1 and 2:

 $(1.66 \text{kW}) \times (24 \text{ hrs /day}) \times (240 \text{ operating days / year}) = 9.56 \times 10^3 \text{ kW per year}$

 $(9.56 \text{ x } 10^3 \text{ kW} / \text{year}) \text{ x } (3.6 \text{MJ} / \text{kW}) = 3.44 \text{ x } 10^3 \text{ MJ} / \text{year}$

 $(3.44 \ 10^3 \text{ MJ} / \text{year}) \text{ x} (1.0 \text{ MJ} / 0.3 \text{ MJ}) = 1.15 \text{ x} \ 10^4 \text{ MJ} / \text{year}$

 $(1.15 \text{ x } 10^4 \text{ MJ} / \text{year}) \text{ x } (8.6 \text{ gC} / \text{MJ}) = 9.89 \text{ x } 10^4 \text{ gC} / \text{year} = 98.9 \text{ kg C} / \text{year}$

(98.9 x kg C / year) x (44g CO₂ / 12g C) = 362 kg CO₂ / year

Therefore, the total relative carbon dioxide emissions for alternative 3 would be similar to that of the current pumping system: $1.94 \times 10^5 \text{ kg CO}_2 / \text{ year.}$

Alternative 4: Relative CO₂ Emissions

The relative carbon dioxide emissions for alternative 4 would have to consider the emissions associated with the current pump system, the powerhouse dry air system, as well as the nitric acid and NOx pump system (negligible). Therefore, the relative carbon dioxide emissions would be very similar to alternative 2 ($2.0 \times 10^5 \text{ kg CO}_2$ / year).

Alternative 5: Relative CO₂ Emissions

The relative carbon dioxide emissions associated with alternative 5 would have to consider the energy power draws for the current pump system, the powerhouse dry air circuit and the ozone generator. The ozone generator would potentially run only once per month. The ozone generator required an average of 121.4kW of power in 2009 [19]. Therefore, following the same steps for previous calculations, the relative carbon dioxide emissions for the ozone generator would be:

(121.4 kW) x (24 hrs / day) x (12 operating days / year) = 3.50×10^4 kW per year

 $(3.50 \text{ x } 10^4 \text{ kW} / \text{ year}) \text{ x } (3.6 \text{ MJ} / \text{ kW}) = 1.26 \text{ x } 10^5 \text{ MJ} / \text{ year}$

 $(1.26 \text{ x } 10^5 \text{ MJ} / \text{year}) \text{ x } (1.0 \text{ MJ} / 0.3 \text{ MJ}) = 4.20 \text{ x } 10^5 \text{ MJ} / \text{year}$

 $(4.20 \text{ x } 10^5 \text{ MJ} / \text{year}) \text{ x } (8.6 \text{ gC} / \text{year}) = 3.61 \text{ x } 10^6 \text{ gC} / \text{year} = 3.61 \text{ x } 10^3 \text{ kgC} / \text{year}$

 $(3.61 \times 10^{3} \text{ kgC} / \text{year}) \times (44 \text{g CO}_{2} / 12 \text{gC}) = 1.32 \times 10^{4} \text{ kgC} / \text{year}$

 $(1.32 \text{ x } 10^4 \text{ kgC} / \text{year}) + (1.94 \text{ x } 10^5 \text{ kg of } \text{CO}_2 / \text{year}) + (5.45 \text{ x } 10^3 \text{ kg of } \text{CO}_2 / \text{year}) =$

 $2.12 \ x \ 10^5 kg$ of CO_2 / year

4.3.8 Alternative 6: Relative CO2 Emissions

The relative carbon dioxide emissions associated with alternative 6 would be very similar to that of the current chloride removal system. As previously mentioned, the relative carbon dioxide emissions associated with the addition of the nitric acid pump to blend the dentration scrubber acid and absorber acid would be negligible. Therefore, the annual relative carbon dioxide emissions would remain around $4.55 \times 10^5 \text{ kg CO}_2$ / year.

Chloride Removal Circuit	Relative Annual CO ₂ Emissions
Current	$4.55 \text{ x } 10^5 \text{ kgCO}_2 / \text{ year}$
Alternative 1	1.94 x 10 ⁵ kgCO ₂ / year
Alternative 2	$2.0 \times 10^5 \text{ kgCO}_2 / \text{ year}$
Alternative 3	$1.94 \text{ x } 10^5 \text{ kgCO}_2 / \text{ year}$
Alternative 4	$2.0 \times 10^5 \text{ kgCO}_2 / \text{ year}$
Alternative 5	$2.12 \text{ x } 10^5 \text{ kgCO}_2 / \text{ year}$
Alternative 6	$4.55 \text{ x } 10^5 \text{ kgCO}_2 / \text{ year}$

Summary: Relative CO₂ Emissions:

Table 11: Summary of Annual Relative CO2 Emissions for the Current and Alternative Chloride Removal Circuits

Carbon dioxide emissions, whether direct or indirect, pose a significant threat for the environment. It is one of the quintessential greenhouse gases that contribute to global warming and the acidification of local water systems [61]. Reducing the carbon footprint of industrial activities embraces not only the direct emission of carbon dioxide, but also the relative emissions associated with energy consumption and lifecycle analyses [62]. Reducing the relative carbon footprint of the BRR is an important consideration for recommending an alternative based on the research performed for this research.

4.4 Operational Impacts Comparison

4.4.1 Nitric Acid Mass Balance

The nitric acid flow rate from absorber B to the chloride circuit is largely dependent on the nitric acid density [42]. Nitric acid density is controlled by altering the flow rate of process water flowing through the nitric acid absorbers (see Section 3.2.3). Nitric acid density of the absorber acid is important for the digestion circuit, since it plays an important role in the uranium dissolution process and the production of uranyl nitrate.

The average flow rate of absorber nitric acid to the chloride circuit is 1.20m³/hr in order to maintain nitric acid strength around 35.0% [42]. There is little flexibility in varying the nitric acid density in the absorber circuit, since the overall mass balance is largely controlled in this area. In order to increase the nitric acid strength of absorber B acid up to 37.0% the density would have to be increased. Reducing the flow of process water through can accomplish higher nitric acid strengths. As a result, the 1.2m³/hr flow rate of absorber B acid to the chloride removal circuit may be reduced as well. However, maintaining the absorber B acid strength around 37.0% will reduce the volume of denitration scrubber acid required to elevate the acid strength to 43.0-44.0% entering the chloride reactors.

The denitration scrubber tanks have a volume of 2.41m³ of strong nitric acid (49.0-50.0%). The flow rate of denitration scrubber acid through the denitration circuit is 56.0m³/hr. Only 1.29m³/hr of denitration acid is pumped to the digestion circuit (this matches the production rate for acid in the denitration scrubber systems). The 56.0m³/hr flow rate through the denitration circuit must be maintained in order to ensure sufficient NOx scrubbing from the off-gases of the denitration pots [42]. Reducing this flow rate could reduce the amount of NOx being scrubbed and ultimately increase the amount of NOx exiting the absorber stack. Therefore, the average flow of denitration scrubber acid that can flow to the chloride circuit is around 1.29m³/hr, since there must be some residual denitration scrubber acid in the tank for surge precautions [42]. The denitration scrubber acid available is what is being produced at the time (the scrubber tank levels are maintained at a set point). One possibility can be to set up an algorithm to control acid flow to the chloride reactors with the flow controller set point varied by the level in the scrubber

tanks. The flow rate of absorber B acid to the chloride removal circuit averages about 1.20m³/hr. Flow from absorber B is also controlled by level [42]. Therefore, there is a sufficient volume of denitration scrubber acid to blend a 1:1 ratio with the absorber acid.

Another important consideration is the nitric acid balance associated with increasing the flow rate of treated nitric acid. Recall that part of the treated acid flows to the nitric acid rundown tank and the other part flows to the solvent extraction process. The flow rate to the solvent extraction process must be maintained in order to avoid deviations to the uranium extraction process. One possibility would be to reroute absorber nitric acid to the solvent extraction circuit prior to entering the chloride removal circuit. However, the nitric acid flow rate to the rundown tank would still increase. The rundown tanks would have to accommodate for this additional volume of nitric acid [42]. The maximum capacity for each nitric acid rundown tank is roughly 20.0m³ (5300 USG). There are two rundown tanks in the nitric acid recovery circuit. Each of the two tanks is maintained at roughly 50% volume of nitric acid. This volumetric balance within each tank is maintained in order to balance the nitric acid throughout the refinery [42]. Therefore, the additional volumetric flow rate of nitric acid entering the rundown tank would have to be routed to the main digestion nitric acid flow control valve. Additional research would be required to test the feasibility of the piping and pumping systems to handle a larger volume of nitric acid through this control valve.

4.4.2 Denitration Process

The first consideration is bleeding denitration scrubber acid into the absorber acid flowing to the chloride reactors. Bleeding nitric acid from the denitration scrubber tank will have to be controlled in order to ensure that a sufficient amount of nitric acid is available to scrub the NOx pipes coming off the denitration pots. This is the primary purpose for the denitration scrubber tank. As discussed previously, if there were insufficient amounts of scrubber acid being pumped through the NOx lines then there would be a drastic increase in NOx gas flowing out the absorber stack from the denitration area. The nitric acid strength of the denitration acid would be unaffected by the alternative chloride removal circuit since it is formed in the denitration area separately. A strong denitration scrubber acid is beneficial, since it is directly pumped to digestion without going through the rundown tank. Therefore, strong denitration scrubber acid benefits the digestion stage of uranium extraction. The nitric acid strength should remain unaffected. Even if the total volume inside the denitration scrubber tank decreases, the nitric acid strength will remain constant. This is due to the fact that the nitric acid strength depends on the flow of denitration

acid through the denitration circuit and not the total volume. The nitric acid is formed outside of the denitration scrubber tank [42].

4.4.3 Loss of Uranium

The third operational consideration is the loss of uranium from the denitration scrubber acid as it passes through the chloride reactors. Under current conditions, part of the denitration scrubber acid flows to the digestion circuit where it is blended into the digested ore entering the extraction column. The uranium contained in the dentration scrubber acid is extracted in the SX circuit. Therefore, an alternative chloride removal circuit that blends the denitration scrubber acid into the absorber acid before entering the chloride removal circuit. However, uranium would have to exit the blended acid passes through the chloride. The conditions in the chloride removal circuit would not be hot enough boil off uranium or uranium bearing products [42]. Therefore, the uranium would remain in the blended nitric acid and would be extracted from the digested ore after it was re-circulated back into the solvent extraction circuit or the rundown tank.

4.4.4 Solvent Extraction Process

A fourth operational consideration is the strength of the nitric acid and uranium concentration within it being pumped to the solvent extraction circuit as it leaves the chloride removal circuit. Recall that part of the treated nitric acid is pumped to the solvent extraction circuit and the rest is pumped to the rundown tank and eventually back to digestion. The alternative chloride removal circuit would increase the nitric acid strength by at least 7.0% up to 43.0-44.0% acid strength and would direct uranium from the denitration scrubber acid into the injection point. Strong nitric acid is a nuisance to the solvent, since it degrades the kerosene/tributyl phosphate mixture and reduces its capacity to extract uranium from the UOCs. A significant amount of the uranium added to the treated solvent would be lost to the raffinate stream [42]. There is an optional pipe to reroute the absorber acid to the solvent extraction circuit prior to entering the chloride reactors. A potential mitigation measure would be to reroute the absorber acid prior to being bled with denitration scrubber acid. This would reduce the amount of acid treated for chloride removal, but would increase the acid concentration inside the chloride reactors, which would result in

improved efficiency. This will be a recommended solution, but it will be more important to dilute this acid prior to addition to the treated solvent, because the untreated acid will have a stronger tendency to degrade the solvent.

5.0 Conclusions and Recommendations

5.1 Conclusions

5.1.1 Summary

This research explored the issue of corrosion and various corrosion reduction methods and technologies currently used in the nuclear fuel manufacturing industry. The BRR presented a unique environment for corrosion due to operating conditions and the nitric acid mass balance that exists within the refinery. A careful analysis of pertinent literature and electrochemical principles revealed that the most effective way to reduce the chloride corrosion problem at the BRR is by oxidizing chloride ions to chlorine gas in the chloride removal circuit. Although the current chloride removal system operates according to this principle, the overall efficiency and cost-effectiveness was low. The current chloride removal circuit uses an ozone generator to pump ozone-rich air through the bottom of each of the three chloride reactors in the removal circuit. The cost to run the ozone generator in 2009 was \$48,948.00. The average ozone composition range achieved in the air being pumped through the chloride removal circuit was 49.0% in 2009. Despite the cost for running the ozone generator, the annual maintenance and repair costs still amounted to \$39,984.02 and \$229,496.16 for the chloride removal and nitric acid recovery circuits respectively.

The goal of this research was to apply an alternative chloride removal system to the BRR that would increase the level of chloride extraction, reduce operating costs, reduce repair costs associated due to corrosion and reduce the environmental impacts. Careful analysis of oxidation electrochemical principles revealed that the conditions in the BRR could be altered to favor the oxidation of chloride in the chloride reactors. Analyzing acquired data on the current chloride removal system revealed that level of chloride extractions greatly increased when the nitric acid strength passing through the reactors from absorber B was above 42.0%. Similarly, chloride concentrations remained constant for absorber B acid strengths between 34.0-37.0%. This information revealed a potential operating range for the alternative chloride

removal circuit. If nitric acid could be maintained at 37.0% out the bottom of absorber B and strengthened to 43.0% entering the chloride removal circuit then up to 90.0% of chloride could potentially be oxidized in the chloride reactors.

Important considerations that were investigated during this research were how to increase the nitric acid strength from 37.0% to 43.0% without affecting the nitric acid mass balance and other operations in the refinery. Careful analysis revealed that slight modifications would have to be done in order to accommodate the changes described for alternatives 1-6. Denitration scrubber acid from the two denitration scrubber tanks was discovered to be the solution for increasing the absorber B nitric acid strength. During the tenure of this research, several scenarios were tested daily in the lab which simulated potential conditions in the refinery. The tested scenarios included five possible volumetric blend ratios of absorber to denitration scrubber acid: 3:1, 2:1, 1:1, 1:2, and 1:3. The five blended acid scenarios were tested for chloride concentrations in order to determine the nitric acid strength threshold for effective chloride removal, which was discovered to be above 42.0%.

A next set of samples were tested by sparging dry air from the powerhouse through each sample for 1.0 minute at 4.0psi. An additional 1:1 blend of nitric acid was sparged with NOx gas for 30.0 seconds at 15psi from the Spencer turbine. Finally, the NOx sparged 1:1 nitric acid blend was sparged with dry air for 1.0 minute at 4.0psi in the laboratory. The various scenarios revealed the effectiveness of six alternatives discussed in Section 3.3. Tables 8 and 9 from section 4.1.3 summarize the average blended nitric acid strengths and level of chloride extractions for the alternatives tested during this research:

The most effective chloride removal scenario was sparging 1:1 blended nitric acid with a combination of NOx and dry air. The combination of NOx and dry air from the powerhouse reduced the chloride concentration an average of 76.7%. This value was lower than the expected stoichiometry due to the testing conditions, but also due to a secondary reaction with nitrous oxide that was not discovered by Pierce et al. (2007). The secondary oxidation reaction between chloride and nitrous oxide was an important gap in the literature that was discovered during this research.

Recall from the study conducted by Pierce et al. (2007) that the level of chloride oxidation increased with temperature [33]. The tests conducted during this research were performed under standard temperature conditions (\sim 50.0 – 30.0°C). The operating conditions in the chloride removal circuit are under much higher temperatures (above 70°C). As a result, the level of chloride extraction could potentially reach as high as 95.0%.

NOx sparging was only tested at a 1:1 volumetric blend ratio, since this was the maximum ratio anticipated for the bleed line from the denitration scrubber tanks. Although ozone was not able to be used for sparging the blended acid, it will likely be higher than NOx and dry air due to the fact that it has the highest ORP value of any oxidant analyzed during this research. Based on Figure 15, using ozone-enriched air can potentially have a level of chloride extraction higher than 95.0%. Total maintenance and repair costs associated with corrosion can be dramatically reduced as a result. Cost savings can be as much as 80.0% (\$215,584.00).

A cost comparison analyzing the operating costs for each alternative revealed that alternatives 2-5 were similar. In comparison to using the ozone generator, alternative 2-5 would reduce energy consumption and operating costs by a minimum of 54.0% (\$45,840.00 saved per year). Careful consideration revealed that each alternative suggested would have minimal operational impacts in terms of the nitric acid mass balance and uranium refining process. Analyzing alternatives 3 and 4, which both use NOx sparging as the primary source of oxidation, revealed that both alternatives would likely not produce adverse environmental impacts if the sparging flow rate was maintained at 2.0kr/hr or less and modifications to the NOx chilling circuit were performed to reduce additional emissions. The relative emission of carbon dioxide was also analyzed during this research. Alternatives 1-5 would reduce the relative carbon dioxide emissions by a minimum of 46.5% (2.11 x 10^5 kg CO₂ per year saved) due to a reduction in energy use. The level of chloride extraction, financial costs, operational and environmental impacts were all considered for recommending an alternative chloride removal system at the BRR.

Another goal of this research was to identify gaps and limitations in current literature regarding chloride extraction methods and provide additional information to this subject. As discussed previously, a limited amount of research has been performed on chloride removal techquiues from nitric acid. The results obtained by Pierce et al. (2007) were valuable for comparison [33]. However, as discussed throughout this research, there were limitations to their research in terms of identifying electrochemical reactions and stoichiometry. The results of this research provided additional information to the subject of chloride oxidation such as the identification of secondary reactions, the importance of ORP values in strong acid, and the effects of several factors on the level of chloride extraction (e.g., trace metals, activation energy).

Also, previous research performed by Wilkinson (1961) suggested that the use of ozone generation as a means to oxidize chloride from nitric acid is both costly and inneficent. Although ozone generation is costly, its efficiency can be significantly increased by strengthening nitric acid prior to being purged with ozone. Wilkinson (1961) did not discuss the factor that nitric acid strength played in the efficiency of chloride oxidation using ozone. The oxidative nature of ozone renders it a highly suitable candidate to be

used as a chloride oxidant. As shown by the results of this research, more than 95.0% of chloride can be extracted from 42.0 - 43.0% nitric acid, which is considered to be a very efficient level of chloride extraction.

5.1.2 General Conclusions

The results obtained from analyzing existing and acquired data for this research revealed that improving the corrosion problem at the BRR can have many positive feedbacks. New corrosion reduction methods or technologies will not be required to reduce the chloride corrosion problem at the BRR. The materials, equipment and circuits already in place can be operated more effectively to increase the level of chloride extraction, reduce costs for electricity, maintenance and repairs, as well as reduce the associated environmental impacts associated with corrosion. An effective operational balance between the absorber nitric acid strength and denitration scrubber acid strength was the solution to corrosion issue at the BRR. There were many operational and environmental considerations taken into account for modifying the current chloride removal system. By controlling the absorber acid strength around 37.0% and increasing the nitric acid strength at the point of entry into the chloride reactors up to 43.0% or higher, the efficiency of chloride removal will drastically increase. Also, monitoring the chloride concentrations in the nitric acid circuit will provide the means to control the amount of ozone generation required (if desired). Improving operational awareness and monitoring will provide the means to control sparging the nitric acid with dry air, NOx and/or ozone depending on the chloride concentrations in the circuit at any given time. This will reduce the chloride corrosion problems, the costs associated with repairs and maintenance to the nitric acid and chloride removal circuits, as well as the environmental impacts associated with the energy and materials demand.

There is a much greater incentive and willingness to reduce environmental impacts when operating conditions and capital costs are reduced coincidentally [63]. This research demonstrated how environmental impacts can be improved without having to rely on modern or improved technology. Material demand and energy consumption are implicated in environmental impacts, capital costs and operating conditions. The goal was to find a medium that improves all three areas similarly. Traditional corporate mentality aims to narrow capital cost margins and overall operating costs. If environmental impacts into this mindset is essential. This research demonstrated how this can be accomplished. Improving the cost-efficiency and overall chloride extraction at the BRR will have benefits on all three levels. First, reducing energy consumption to the chloride removal circuit will reduce the overall operating costs.

and thus reduce the carbon footprint of the BRR. Lastly, reducing chloride concentrations will reduce the material demand to repair corroded steel and equipment in the nitric acid circuit. Again this is beneficial operationally, financially and environmentally.

This research strongly embraced the idea of presenting a range of alternatives based on existing conditions at the BRR. The introduction and literature review presented the issue of corrosion, the relevant methodological and electrochemical principles, and a thorough presentation of the case study. The alternatives for this research embraced these concepts and were designed to provide a range of possibilities for the case company to consider. Each alternative contains strengths and weaknesses in various areas. Alternatives are the most essential component of project (when considering environmental impacts), since they provide multiple options to carry out a specific goal [64]. Ultimately, the environmental impact assessment is assessing which alternative has the least environmental impacts associated [64]. This point presented by Marriot (1997) was considered in this research for recommending an alternative to the BRR. However, operational and financial impacts were also major considerations in the decision.

It is ultimately the discretion of the case company to consider which alternative meets their goals and priorities. For example, utilizing the ozone generator in combination with the dry air circuit, as opposed to only sparging the chloride reactors with the dry air, will reduce the overall concentration of chloride in the refinery and ultimately the level of repairs, maintenance and materials required. However, this alternative would also require a much greater energy demand, which has operational, financial and environmental impacts associated with it. Therefore, the BRR must balance their goals of reducing chloride concentrations, repairs and maintenance costs, and environmental impacts.

In comparison to Marriot (1997), George and Lee (2000) argue that the most important consideration for a project is predicting the environmental impacts associated with an undertaking [65]. In order to predict potential environmental impacts, George and Lee (2000) argue that a thorough understanding of the surrounding environment is required in order to predict the impacts as accurately as possible [65]. Environmental impact prediction and cumulative effects were considered for this research. Alternatives 3 and 4 raised concerns due to the fact that NOx, nitrate and nitrite levels would increase as a result of NOx sparging through the chloride reactors. A brief cumulative impact assessment was performed from 2000 to 2005 when nitrate and nitrite concentrations were above the concentrations that would result from alternatives 3 and 4. Careful analysis revealed that rainbow trout, a highly sensitive species to nitrate and nitrites, were unharmed when concentrations of nitrate and nitrite were slightly higher than the ones that would result from alternatives 4 during the period of 2000 to 2005. Therefore, drastically reducing the

energy consumption for the current chloride removal circuit and reducing the materials required to continuously repair corrosion damage at the BRR will produce positive environmental impacts over the long-term.

This research embraced many concepts presented in the Pollution Prevention course for the Environmental Applied Science and Management Masters program at Ryerson University. The following concepts were considered while conducting this research: energy efficiency, economics of pollution prevention, indicators and metrics, and the concept of value [63]. Energy efficiency was a major consideration for this research. The cost-effectiveness of the current chloride removal circuit was low in terms of energy efficiency. Increasing the nitric acid strength through the chloride removal circuit will undoubtedly increase the efficiency of chloride extraction, since the overall concentration of chloride will be reduced. It will also increase the energy efficiency due to the fact that the ozone generator will be run less frequently (if at all). The combination of ozone, NOx and/or dry air will reduce the energy consumption of the chloride removal circuit, while increasing the level of chloride extraction. This will also reduce the cost of materials and maintenance required to repair the corrosion damage posed by high chloride concentrations. This is a three-fold positive effect that creates a huge incentive for the BRR to implement an althernative chloride removal circuit based on the results of this research. This concept strongly reflects the concept of pollution prevention economics. Upper management personnel are much more incline to adopt pollution prevention programs when there are financial incentives associated with them. The three-fold benefits associated with the alternatives suggested in this research provides the financial incentive required for implementation [63].

Operational indicators will play an important role in guiding the operation of the alternative chloride removal circuit [63]. A chloride mass balance was performed with the goal of obtaining information to create an operational indicator for the alternative chloride removal circuit. The initial goal was to develop a checklist of ore feeds into the BRR circuit. A chloride concentration profile of the UOCs being fed into the circuit would guide the operation of either the ozone generator, NOx fume line, and/ or the dry air line. However, the UOC chloride concentrations had major variations and the blended ores fed into the circuit render this indicator a poor option. Therefore, the chloride concentration in the absorber B nitric acid will serve as the primary operational indicator driving the use of the ozone generator or one of the alternatives.

Based on the results and conclusion discussed in the previous two sections, the following section will present the recommendations for altering the chloride removal circuit at the BRR. The recommendations will encompass all of the impacts considered during this research. The recommended alternative(s) and

associated operational modifications will be derived by analyzing an effects matrix that encompasses the major considerations for the BRR.

5.2 Recommendations

5.2.1 Impact Matrix: Recommendation of Alternative(s)

The following impact matrix was used as the primary criteria for recommending an alternative from the list provided in section 3.3:

Alternative	Chloride Removal	Total Costs	Environmental Impact	Operational Impact
1	0	3	0	3
2	0	3	0	3
3	4	3	2	3
4	5	3	2	3
5	3-5	3-5	1	3
6	5	5	3	0

Table 12: Impact Matrix: The following table measured the impacts associated with each alternative considered in this research. Note: 0 = no effects; 1 = negligible effects; 2 = minimal effects; 3 = moderate effects; 4 = significant effects; and 5 = major effects.

The first criterion was rated based on the current chloride removal circuit. Alternatives 1 and 2 could potentially increase the overall level of chloride reduction compared to the use of ozone. But, as shown from the lab tests, this may not be the case. Nitric oxide, nitrous oxide and ozone were the strongest oxidants of all the alternatives and have the highest potential of removing chloride from the nitric acid. Therefore, alternatives 4 and 6 could potentially double the level of chloride extraction compared to the current circuit. Alternative 5 included a combination of dry air and ozone to reduce chloride concentrations. Depending on the frequency of ozone use, the level of chloride extraction could be dramatically increased. The second indicator represented the total costs of implementing the alternative. The total costs included: capital costs, energy costs, as well as maintenance and repair costs.

The third indicator represented the overall environmental impacts associated with each alternative. The environmental impact rating was based on the reduction of energy use, relative carbon dioxide emissions and material requirements versus the environmental toxicants released for each alternative: ozone, NOx, nitrates and nitrites. Alternatives 1 and 2 were assigned with the lowest environmental impact rating due to the fact that ozone would be completely reduced and NOx, nitrate and nitrite levels would remain the same (or reduced if modifications were performed to the NOx chilling system). Alternatives 3 and 4 were allocated a rating of 2 due to the debate between the increase in NOx, nitrite and nitrate emissions versus the environmental impact associated with high energy and material use. The relative increase in NOx, nitrate and nitrite emissions were deemed to be low in comparison to the energy and material reductions associated with reducing the level of corrosion at the BRR. Also, the fact that NOx, nitrate and nitrite emissions could be reduced with modifications to the NOx chillin system provided rationale for assigning a low value in terms of environment limpacts.

The fourth indicator represented the degree of operational impacts for each alternative. The list of potential operational impacts was discussed in section 4.4 and included: nitric acid mass balance, denitration process, loss of uranium, and solvent extraction process. This indicator demonstrated the level of modifications required to the operations and circuits at the BRR to accommodate for the alternative.

Based on the results of the impact indicator matrix a combination of alternatives 4 and 5 would be the best scenario to apply to the BRR refinery. The chloride removal circuit can be sparged with air from the powerhouse pumps during the entire operational year. Then, sparging the nitric acid with either NOx or ozone (not at the same time) can be performed periodically based on the chloride concentration in the absorber acid. If NOx, nitrate and nitrite concentrations are high in the off-gas scrubber system, aeration tank or plant effluent discharge (discretionary) when the chloride concentration in absorber B acid is above 450.0 - 500.0mg/L, then (and only then) the ozone generator could be powered and sparge the nitric acid with ozone-enriched air. The maximum flow rate of NOx to the bottom of the eductor pumps would be 2.0kg/hr. The air drier should only be operated only when the ozone generator is running.

In order to accomplish the desired nitric acid strength through the chloride reactors, a bleed line will have to be added from the denitration scrubber tanks to the absorber B line as close to the chloride reactors as possible. The flow of nitric acid from the absorber stream and denitration scrubber acid stream can be oriented so that they would combine in the first chloride reactor. The flow of denitration scrubber acid to the chloride removal circuit will have to match the flow rate of the absorber acid in order to achieve a 1:1 volumetric blend ratio. The flow rate of blended acid through the chloride reactors should be around 2.0m³/hr, which means that1.0m³/hr of absorber B acid and 1.0m³/hr of denitration scrubber acid would be required.

A 1.0" or 1.1/2" NOx fume line should be added from the Spencer turbine to the eductor pumps at the bottom of each chloride reactor. The chloride concentration threshold range for opening the NOx fume line or turning on the ozone generator to flush out additional chloride should be a nitric acid absorber chloride concentration between 450.0-500.0mg Cl/L. Only the air pump should be run when chloride concentrations are below this range. However, this is at the discretion of BRR management.

Absorber B nitric acid should be rerouted to the solvent extraction circuit prior to being bled with denitration scrubber acid in order to reduce the amount of process water required to dilute the acid in the solvent extraction ncircuit and avoid the loss of uranium. All of the treated acid can be routed to the rundown tank as it leaves the chloride removal circuit. Applying these recommendations can increase the level of chloride extraction from 49.0% currently to as high as 90.0 - 95.0%. This would greatly increase the cost-effectiveness of the chloride removal circuit and all of the associated impacts discussed in this research.

5.2.2 Nitric Acid Concentrator Circuit Modifications

The initial goal of installing the chloride removal circuit at the BRR was to remove chloride from the concentrator nitric acid stream. Although this research is intended to provide an alternative means of removing chloride from the absorber nitric acid stream, operational modifications can be applied to the concentrator circuit to reduce the concentrator of chloride. The most effective way of indirectly reducing the chloride concentration in the concentrator circuit is maintaining nitric acid strength below 37.0% in order to flush out chloride ions. Flushing out the chlorides is essential for reducing the overall concentration of chloride in this area over time. Chloride in the concentrator acid will ultimately end up in the nitric acid rundown tank and flow through the circuit. Part of that concentration will end up in the absorber acid, which will flow through the chloride removal circuit. Over time the chloride concentrations in the nitric acid concentrators would drop due to the elimination of additional chlorides in the chloride removal circuit.

5.3 Contributions and Benefits to the Case Company

The contributions to the BRR are not only associated with reducing the overall chloride concentration in the nitric acid circuit. There are multiple contributions and benefits that may result from this research:

- A better understanding of chloride sources and circulations throughout the entire refinery.
- An improved chloride removal yield in the chloride removal circuit. Thus, this will reduce the overall maintenance and repair costs associated with corrosion damage in the refinery.
- Improved operational awareness for the chloride removal circuit. Understanding which conditions and feeds will either cause high or low chloride concentrations can be used to operate the ozone generator or simply purge the chloride reactors with dry air. This will reduce the overall operational costs of the chloride removal circuit and increase the cost-efficiency of chloride removal at the BRR.
- Reducing the use of the ozone generator will provide positive environmental impacts such as: reduced ozone potentially leaking into the environment; reduced energy requirement and hence reduced relative CO₂ emissions; and reduced material requirements associated with the repairs and maintenance to the nitric acid and chloride removal circuits.
- Minimal operational impacts associated with the modifications to the chloride removal system.

5.4 Contributions to the Academic Knowledge Base

The contributions to the academic knowledge base are not only associated with reducing corrosion of stainless steel. There are multiple other contributions to the academic knowledge base that may result from this research:

- An improved understanding of chloride corrosion of stainless steel.
- An improved understanding of the significance and range of impacts corrosion can have on a particular industrial site.
- An expanded knowledge on the various chloride removal techniques and methods that can be applied in the nuclear fuel manufacturing industry and which techniques and methods are best suited for specific environments.

- An improved understanding of chloride removal techniques and methods, as well as a better understanding of the degree of difficulty and wide range of considerations required for a particular practice.
- An improved understanding of thermodynamic and electrochemical principles associated with chloride corrosion reduction.
- Additional theoretical information that built on previous research, such as Pierce et al. (2007), and provided an understanding of previous gaps and litmitations (i.e., secondary oxidation reactions, ORP values, oxidation behavior at various acid strengths, effects of contaminants).
- Empirical evidence that built on previous research, such as Wilkinson (1961), and demonstrated that the efficiency of oxidants used for chloride extraction can be significantly increases with higher nitric acid strengths.
- Much needed research in the area of chloride extraction from nitric acid, which will provide useful literature for future academic research in similar areas.

5.5 Recommendations for Future Research and Monitoring

Based on the results obtained during this research and the effects that must be considered to efficiently operate an alternative chloride removal system the following recommendations should be considered for future research at the BRR:

- Continuously monitor and sample the wet scrubber tank, aeration (blowdown) tank, plant effluent discharge for nitrite levels, as well as the absorber stack for NOx emissions. If these concentrations are high then close the NOx fume line to the chloride reactors and run the ozone generator instead if needed.
- Conduct an internal study to investigate modifications to the chiller and off-gas scrubber systems to reduce the slight increase in NOx emissions out of the absorber stack and nitrate/nitrite levels in the plant effluent discharge.
- Conduct an internal research that investigates possible vessels that can be used to withstand the NOx/chlorine concentrations from blending denitration scrubber acid with absorber acid. Investigate the possible locations that a new vessel can be built in order for the blended acid to flow into the first chloride reactor.

- Conduct an internal research that investigates the flow and volumetric capacity of the chloride reactors and associated pumping systems in order to ensure that doubling the flow rate of nitric acid through the removal circuit can be accommodated.
- Conduct an internal research that investigates the implications of having additional nitric acid flowing out of the rundown tanks due to the increased input of treated acid. The main consideration could involve the current project investigating the production capacity increase from 18,000 tons to 24,000 tons of uranium trioxide per year. The research could investigate the capacity of the piping and pumping system to accommodate for the additional nitric acid flow, as well as the capacity of the piping and pumping system to handle an increase of nitric acid flow.
- Conduct an internal research that investigates operational conditions that can maintain a denitration scrubber acid strength above 50%. This will be largely beneficial to the proposed chloride removal circuit since either a lower volume of denitration scrubber acid will be required to elevate the nitric acid strength from 37-38% to 43-44% or if the same volume of denitration scrubber acid is bled in then the nitric acid strength can be potentially raised above 45%.
- Conduct further academic research exploring the ORP values of oxidants (e.g., nitric oxide, nitrous oxide, ozone) at specific acid strengths.
- Conduct further academic research exploring the level of chloride extraction from different strong acids (e.g., sulphuric, hydrofluoric), as well as their application in various industries.
- Conduct further industrial and academic research exploring the use of chloride absorption (e.g., use of chromium) as a means to extract chloride from strong acids.
- Conduct further academic research exploring other strong oxidants that are present in strong acids (e.g., sulphuric, hydrofluoric) that can be used to extract chloride in a similar way as presented in this research.

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APPENDIX A: ACRONYMS AND DEFINITIONS

ACRONYMS

ATSD: Agency for Toxic Substances and Disease **BRR:** Blind River Refinery **CCME:** Canadian Council of Ministers of the Environment **CEAA:** Canadian Environmental Assessment Agency **CEPA:** Canadian Environmental Protection Act **CNSC:** Canadian Nuclear Safety Commission **D-Raff:** Dilute Raffinate EC: Environment Canada IESO: Independent Electricity System Operator **IUPAC:** International Union of Pure and Applied Chemistry MISA: Municipal and Industrial Strategy for Abatement **MOE:** Ministry of the Environment NOx: Oxides of Nitrogen **ORP**: Oxidation-Reduction Potential $(E^{\circ}(V))$ **PFD:** Process Flow Diagram **Redox:** Oxidation-Reduction **SCC:** Stress Corrosion Cracking **SX:** Solvent Extraction **UNH:** Uranyl Nitrate Hexahydrate **UOC**: Uranium Ore Concentrate **UV-Spec:** Ultraviolet-Visible Spectrometer

DEFINITIONS

Acid Strength: The ability of an acid to lose a proton. Strong acids are characterized by completely dissociating in water, whereas weaker acids only partially dissociate. The acid strength of an acid is a function of molarity, density and molecular weight. It is measured as a percentage (%) [35].

Activation Energy: The minimum energy required for a chemical reaction to take place. It is measured as the difference between the maximum energy and the energy of the reactants. It is generally measured in joules per mol (J/mol) of reaction [35].

AS 400: Blind River Refinery internal data input system. It contains all sample points, determinants and results for all analytical tests conducted at the refinery [42].

Ammonium Sulphate: $(NH_4)_2SO_4$. An inorganic salt used to bind to calcium cations for the UV-visible spectrometer readings. Calcium interferes with the UV-Spec readings for chloride concentrations, since they are able to absorb 460nm UV light [38].

Arrhenius Equation: An equation developed by Swedish chemist Svante Arrhenius in the late 19th century. The equation is used to determine the way in which the rate of a chemical reaction varies with temperature.

lnK = lnA - Qc/RT

Where K is the rate of a given constant; A is the pre-exponential factor; Ea is the activation energy; R is the gas constant; and T is the temperature. The pre-exponential factor (A) is determined experimentally [36].

Carbon Intensity: The amount of carbon emitted per unit of energy consumed. It is generally measured in grams of carbon emitted per megajoule of energy (gC/MJ) [58].

Chloride/Chlorine: Chlorine is the chemical element with the atomic number 17. It is part of the halogen gas family and is denoted by Cl. Chloride is the ionic form of chlorine when it is dissolved in an aqueous solution. It is denoted by Cl⁻ [35].

Crevice Corrosion: A form of corrosion associated with an immobile fluid. It is generally observed in shielded areas such as beneath washers, gaskets, and threads [4].

Corrosion: The deterioration of a material into its elemental constituents due to chemical reactions with its environment. The most common corrosion reaction is electrochemical oxidation, whereby a material reacts with an oxidant such as oxygen or chlorine to produce metallic oxides [35].

Density: The concentration measured as mass per unit of volume. The most common measurements are grams per liter (g/L) and kilograms per cubic meter (kg/m^3) [35].

Electrochemical Series: A series in which metals and other substances are listed in the order of their chemical reactivity or electrode potentials. The series is structured by arranging the most reactive at the top and the less reactive at the bottom. It is also commonly referred to as the Electromotive Series [35].

General Corrosion: A form of corrosion that proceeds in a relatively uniform manner over the entire surface of a metal. Typically, stainless steels do not exhibit general corrosion [3].

LC50: Median lethal concentration that cause fatality in 50.0% of the test population [55].

Mercuric Thiocyanate: An inorganic salt of mercury. It is used for the determination of chloride concentrations by UV-visible spectrometry. Mercuric thiocyanate is added to a solution with an unknown concentration of chloride ions. Mercuric thiocyanate reacts with iron chloride to form the secondary compound $Fe(SCN)^{2+}$. This compound is used to measure the concentration of chloride since it is formed as a result of the extent of the reaction between chloride ion and mercury thiocyanate as an equivalency [38].

Molarity: The molar concentration of a solute in a solution. It is measured as number of moles per unit volume (e.g., mol/L) [35].

Nitrate: NO₃⁻ ion. It is the conjugate base of nitric acid dissociation in solution [35].

Nitric Acid: HNO₃. It is a strong inorganic acid that is a highly reactive oxidizing agent used in the production of fertilizers, explosives, and rocket fuels and in a wide variety of industrial metallurgical processes. It is transparent, colorless to yellowish, fuming corrosive liquid that is also known as aqua fortis [35].

Nitric Oxide: NO. It is the binary compound between nitrogen and oxygen. It is a strong oxidant that readily oxidizes in the presence of air [35].

Nitrous Oxide: N_2O . Under standard conditions, it is a colorless non-flammable gas with a sweet odor. It is commonly known as laughing gas [35].

Nitrous Acid: HNO₂. It is a weak inorganic acid that only exists in solution or in the form of its nitrite salt [35].

Nitrite: NO₂⁻ ion. It is the conjugate base of nitrous acid dissociation in solution [35].

Normality: A measure of substance equivalents that are dissolved in a volume of solution. It is the molarity of a solution multiplied by the number of moles of that substance that occur in a chemical equation. E.g., nitric acid dissolves an equivalent of 1 mol of hydrogen to 1 mol of its conjugate salt. Therefore, normality and molarity for nitric acid are the same value [35].

Oxidation: A chemical reaction where an element or material undergoes a loss of an electron(s) or a gain of an oxygen molecule [35].

Oxidation-Reduction Potential: Electrical charge measured for a particular oxidation-reduction reaction. The charge measures the voltage created by the transfer of electrons. It is measured as E^o in volts (V) [35].

Ozone: O_3 . It is a molecule containing three oxygen atoms. It is an allotrope of oxygen and is a strong oxidant gas [35].

Passivation: Process where stainless steel is submerged in a solution of nitric acid, or nitric acid and oxidizing salts, which reacts to form a corrosion resistant surface by forming a thin transparent oxide film [35].

pH: The logarithm of the reciprocal of hydrogen ion concentration in gram atoms per liter. The pH is measured on a scale from 0 to 14 to denote the acidity or alkalinity of a solution. A pH of 7 is neutral; greater than 7 is more basic; and less than 7 is more acidic [35].

Pitting Corrosion: A specific localized form of corrosion that produces small holes in the affected material. It is caused by a lack of oxygen in the affected area [4].

Potassium Oxalate: $K_2C_2O_4$ · H_2O . It is an odorless, colorless, water soluble crystal that decomposes when heated. It is generally used in analytical chemistry as an oxalic acid conjugate base [40].

Purge: An act of removing by cleansing or ridding of undesired elements [35].

Relative Carbon Dioxide Emission: The amount of carbon dioxide emitted indirectly by an activity or operation. It is generally measured in kilograms of carbon dioxide per unit of time [58].

Sparge: The injection of a gas into a solution (e.g., sparging water with air) [35].

Stress Corrosion Cracking (SCC): A form of corrosion where cracks slowly form in stainless steel due to mechanical stress and exposure to a corrosive environment (such as high temperature, low pH or a high concentration of a strong oxidant) [15].

UV-Visible Spectrometer: A spectrometer that is commonly used in remote sensing that measures spectra in the ultra-violet (UV) to visible waveband. It is used to derive concentrations of elements of interest in particular solutions for materials [38].